



ADVANCES IN ORGANOMETALLIC CHEMISTRY

Volume 11

F. G. A. Stone &
Robert West

Advances in
ORGANOMETALLIC CHEMISTRY

VOLUME II

ADVISORY BOARD

H. J. EMELÉUS

HENRY GILMAN

CONTRIBUTORS TO THIS VOLUME

Herbert C. Brown

M. I. Bruce

P. J. Craig

C. S. Cundy

B. M. Kingston

M. F. Lappert

Alexander McKillop

J. M. Pratt

Edward C. Taylor

Paul M. Treichel

D. R. Wiles

Andrew Wojcicki

Advances in **ORGANOMETALLIC CHEMISTRY**

EDITED BY

F. G. A. STONE

DEPARTMENT OF INORGANIC CHEMISTRY
THE UNIVERSITY
BRISTOL, ENGLAND

ROBERT WEST

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN

VOLUME II



1973

ACADEMIC PRESS

New York • London

COPYRIGHT © 1973, BY ACADEMIC PRESS, INC.
ALL RIGHTS RESERVED.
NO PART OF THIS PUBLICATION MAY BE REPRODUCED OR
TRANSMITTED IN ANY FORM OR BY ANY MEANS, ELECTRONIC
OR MECHANICAL, INCLUDING PHOTOCOPY, RECORDING, OR ANY
INFORMATION STORAGE AND RETRIEVAL SYSTEM, WITHOUT
PERMISSION IN WRITING FROM THE PUBLISHER.

ACADEMIC PRESS, INC.
111 Fifth Avenue, New York, New York 10003

United Kingdom Edition published by
ACADEMIC PRESS, INC. (LONDON) LTD.
24/28 Oval Road, London NW1

LIBRARY OF CONGRESS CATALOG CARD NUMBER: 64-16030

PRINTED IN THE UNITED STATES OF AMERICA

Contents

LIST OF CONTRIBUTORS	ix
ERRATUM	xi

Boranes in Organic Chemistry

HERBERT C. BROWN

I. Introduction	1
II. Diborane as a Reducing Agent	3
III. Volatile Compounds of Uranium	4
IV. The Alkali Metal Hydride Approach to Diborane	5
V. Alkali Metal Borohydrides	6
VI. Molecular Addition Compounds and Steric Strains	7
VII. Steric Assistance in Solvolysis	8
VIII. The Nonclassical Ion Problem	9
IX. Selective Reductions	11
X. Hydroboration	12
XI. The Versatile Organoboranes	14
XII. Conclusion	17
References	18

Transition Metal-Isocyanide Complexes

PAUL M. TREICHEL

I. Introduction	21
II. Structure and Bonding	23
III. Current Topics	28
IV. Isocyanide Complexes of Various Metals	49
References	81

Insertion Reactions of Transition Metal-Carbon σ -Bonded Compounds I: Carbon Monoxide Insertion

ANDREW WOJCICKI

I. Introduction to and Scope of Insertion Reactions	88
II. Carbon Monoxide Insertion. General Considerations and Background	90
III. Kinetics and Mechanism of Carbon Monoxide Insertion	94
IV. Kinetics and Mechanism of Decarbonylation	105
V. Stereochemistry of Carbonylation and Decarbonylation	112
VI. Survey of Reactions	117
References	139

Recent Advances in Organothallium Chemistry

ALEXANDER McKILLOP and EDWARD C. TAYLOR

I. Introduction	147
II. Organothallium(I) Compounds	148
III. Organothallium(III) Compounds	155
References	202

The Radiochemistry of Organometallic Compounds

D. R. WILES

I. Introduction	207
II. Chemical Effects of Nuclear Transformations	208
III. Survey of Experimental Results	221
IV. Discussion	237
References	249

Organometallic Complexes with Silicon-Transition Metal or Silicon-Carbon-Transition Metal Bonds

C. S. CUNDY, B. M. KINGSTON, and M. F. LAPPERT

I. Introduction	253
II. Organometallic Complexes with Silicon-Transition Metal Bonds	254
III. Transition Metal-Catalyzed Homogeneous Hydrosilylation	297
IV. Organometallic Complexes with Silicon-Carbon-Transition Metal Bonds	310
References	323
References Added in Proof	330

Preparation and Reactions of Organocobalt(III) Complexes

J. M. PRATT and P. J. CRAIG

I. Introduction	332
II. Coordination Chemistry	341
III. Formation of the Co—C Bond	350
IV. Preparative Methods	361
V. Reactions and Equilibria Not Involving Cleavage of the Co—C Bond	396
VI. Cleavage of the Co—C Bond	401
VII. Catalytic and Enzymatic Reactions	433
References	441

The Literature of Organo-Transition Metal Chemistry 1971

M. I. BRUCE

A. New Textbooks	448
B. Reviews	450
C. Primary Journals	451

Contents

vii

D. Abstracting Journals	451
E. Conferences	451
F. Synthesis	454
G. Data Compilations	454
Reference	455
Appendix	455
AUTHOR INDEX: REVIEWS OF ORGANO-TRANSITION METAL CHEMISTRY	469
AUTHOR INDEX	472
SUBJECT INDEX	499
CUMULATIVE LIST OF CONTRIBUTORS	507
CUMULATIVE LIST OF TITLES	509

This Page Intentionally Left Blank

List of Contributors

Numbers in parentheses indicate the pages on which the authors' contributions begin.

- HERBERT C. BROWN (1), *Department of Chemistry, Purdue University, Lafayette, Indiana*
- M. I. BRUCE (447), *Department of Inorganic Chemistry, The University, Bristol, England*
- P. J. CRAIG (331), *School of Chemistry, City of Leicester Polytechnic, Leicester, Leics, England*
- C. S. CUNDY (253), *School of Molecular Sciences, University of Sussex, Brighton, England*
- B. M. KINGSTON¹ (253), *School of Molecular Sciences, University of Sussex, Brighton, England*
- M. F. LAPPERT (253), *School of Molecular Sciences, University of Sussex, Brighton, England*
- ALEXANDER MCKILLOP (147), *School of Chemical Sciences, University of East Anglia, Norwich, England*
- J. M. PRATT (331), *Imperial Chemical Industries Ltd., Corporate Laboratory, Runcorn, Cheshire, England*
- EDWARD C. TAYLOR (147), *Department of Chemistry, Princeton University, Princeton, New Jersey*
- PAUL M. TREICHEL (21), *Department of Chemistry, University of Wisconsin, Madison, Wisconsin*
- D. R. WILES (207), *Chemistry Department, Carleton University, Ottawa, Canada*
- ANDREW WOJCICKI (87), *Department of Chemistry, The Ohio State University, Columbus, Ohio*

¹ Present address : Careers & Appointments Advisory Service, University of Edinburgh, Edinburgh, Scotland.

This Page Intentionally Left Blank

Erratum

VOLUME 10

Page 437 (Author Index).

First two lines in entry for D. M. Ritter should be changed to read:

Ritter, J. J., 247, 249(85), 250(84), 251(84), 252(28), 253(84,88),
254(27,

Entry for D. M. Ritter should read:

Ritter, D. M., 249(30), 270

This Page Intentionally Left Blank

Boranes in Organic Chemistry*

HERBERT C. BROWN

*Department of Chemistry
Purdue University
Lafayette, Indiana*

I. Introduction	1
II. Diborane as a Reducing Agent	3
III. Volatile Compounds of Uranium	4
IV. The Alkali Metal Hydride Approach to Diborane	5
V. Alkali Metal Borohydrides	6
VI. Molecular Addition Compounds and Steric Strains	7
VII. Steric Assistance in Solvolysis	8
VIII. The Nonclassical Ion Problem	9
IX. Selective Reductions	11
X. Hydroboration	12
XI. The Versatile Organoboranes	14
XII. Conclusion	17
References	18

I

INTRODUCTION

Recent developments have persuaded me that we may be doing the current generation of graduate students in chemistry a disservice by our failure to transmit to them a better knowledge of the background of our science. At one time there were many more graduate courses. These were presented more leisurely and there was time to discuss how major developments had arisen, as well as stories of individual chemists, their difficulties in getting started, and the methods used to overcome the experimental difficulties they faced. This historical background provided a valuable asset for the new generation of students facing similar problems.

Unfortunately, this background is no longer an accepted part of graduate education. The rapid pace of chemical developments in the past two decades has resulted in major changes in the nature of graduate education in

* Based upon the Roger Adams Award Address to the Division of Organic Chemistry of the American Chemical Society in Ann Arbor, Michigan, June 15, 1971.

chemistry, changes which have had the effect of squeezing such historical background from the program. There are few courses and very little, if any, time is devoted to acquainting the student with historical background. Instead, the emphasis is placed on self-education of the student through reading the current literature. Consequently, many of our younger colleagues are lacking the kind of historical perspective that was an accepted part of the education of chemists of earlier generations.

As I have observed the current scene, it has seemed to me that this failure to transmit previous experience is having a particularly serious impact on the current group of chemists now beginning their careers. They are appalled by the current difficulties in obtaining positions or in raising adequate research funds, difficulties that were accepted as normal by chemists in the past. If these new graduates cannot obtain all the equipment they would like, they become discouraged. They fail to recognize that many chemists have faced this problem previously and have utilized their imagination to achieve major advances with inadequate equipment.

Consequently, I was especially receptive to the invitation from the Editors of *Advances in Organometallic Chemistry* to write an historical review of our researches involving boranes in organic chemistry. Perhaps we will witness a renewed effort to acquaint the student with the historical background so that he can face the problems of the present and the future with a greater confidence based upon some knowledge of how these problems were faced and often overcome by earlier workers.

I recently included much of this personal background in the Roger Adams Award Address on which this chapter is largely based. However, space limitations made it impossible to include this personal background in the present chapter.¹ Consequently, I decided to review our research program in the borane area over the past 35 years with emphasis on the factors which led us to each new development.

There is often a feeling in the young that most of the important things in chemistry have already been discovered and explored. I felt that way in 1938, when I received my own degree. As a result of my own experiences, I have altered my position. Perhaps this discussion of our research program over the past 35 years will help persuade others of the validity of my present belief that we are surrounded by major new areas awaiting discovery.

¹ However, I have attempted to do so in a book under the same title, *Boranes in Organic Chemistry*, Cornell University Press, Ithaca, New York, 1972.

II

DIBORANE AS A REDUCING AGENT

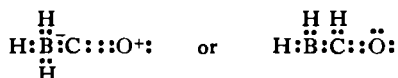
I began graduate studies at the University of Chicago in 1936. At that time, the structure of diborane was a subject of considerable study and



speculation (1). The late Professor H. I. Schlesinger was studying the reactions of diborane in the hope of obtaining information that would throw light on the problem of the structure. At the time I began, the synthesis of borane-carbonyl had just been completed (2). There was

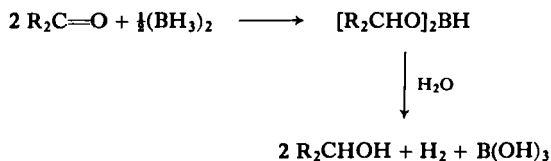


discussion as to whether borane-carbonyl was best represented as a simple addition compound, or whether the reaction involved migration of a hydride



moiety from boron to carbon. It was suggested that I undertake a study of the reaction of diborane with aldehydes and ketones in the hope the results would contribute to a decision as to the structure of borane-carbonyl.

I soon discovered that simple aldehydes and ketones react rapidly with diborane at 0° C. Hydrolysis then produces the corresponding alcohol.



My thesis was completed in 1938 and the results were published in 1939: Hydrides of Boron. XI. The Reaction of Diborane with Organic Compounds Containing a Carbonyl Group (3).

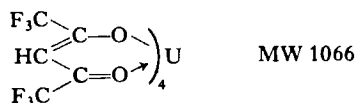
Interest in this development among organic chemists was minimal. Diborane was a chemical rarity at the time, available only in milligram quantities through complex procedures.

III

VOLATILE COMPOUNDS OF URANIUM

This situation was altered late in 1941 as a result of pressures engendered by World War II. Professor Schlesinger was asked by an agency of the Government to undertake a research program on the preparation of new volatile compounds of uranium. I had become his research assistant in 1939, so I became associated with this program.

Originally we undertook to prepare uranium(IV) acetylacetonates and related derivatives. Indeed, the hexafluoroacetylacetonate possessed



promising characteristics. However, when we happily reported this development the blow came. We were informed that there was a little requirement of which we had not been informed previously. It was necessary that the compound have a low molecular weight, preferably not higher than 238! Clearly this approach was not practical.

Just prior to this time aluminum borohydride (4) and beryllium borohydride (5) had been prepared in our laboratories. These are the most



volatile known compounds of beryllium and aluminum. Accordingly, it was decided to undertake the preparation of uranium borohydride, $\text{U}(\text{BH}_4)_4$.

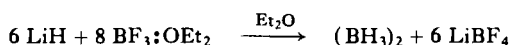
In the usual high-vacuum apparatus I placed aluminum borohydride onto a sample of uranium tetrafluoride. I observed an immediate reaction, with formation of green crystals which could be moved about the vacuum apparatus. As it happened, on the very day I was performing the synthesis, we had a visit from Professor H. C. Urey, who was in charge of the overall study. He immediately asked us to increase our research effort and undertake to prepare uranium tetraborohydride on a relatively large scale, adequate for testing.

IV

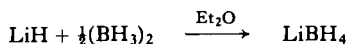
THE ALKALI METAL HYDRIDE APPROACH TO DIBORANE

At this time the only known routes to diborane were that introduced by Stock involving hydrolysis of magnesium boride (1) and that developed by Schlesinger and Burg involving the reaction of boron trichloride with hydrogen in the silent electric discharge (6). These methods made diborane available in relatively small quantities, inadequate for our requirements in synthesizing uranium(IV) borohydride in the desired quantity. Consequently, we were forced to consider new approaches.

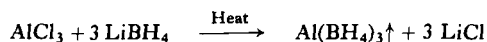
We soon discovered that lithium hydride would reduce boron trifluoride in ethyl ether solution to give diborane (7).



Lithium hydride added diborane to form lithium borohydride (7).



Lithium borohydride reacted with aluminum chloride to produce aluminum borohydride (7).



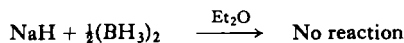
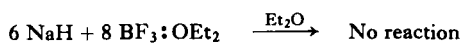
Finally, uranium borohydride could be produced by the method we had originally used (7).



This was obviously a major improvement over the original procedure, which involved many more steps, some of them quite difficult. We happily reported this improved synthesis and undertook to use it to produce uranium(IV) borohydride for large-scale testing.

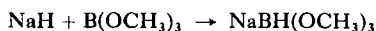
We were then informed that lithium was in very short supply and could not be used on a commercial scale. On the other hand, the supply of sodium was ample. Consequently, we had to find a route through sodium hydride.

Unfortunately, the same reactions failed to proceed with sodium hydride.

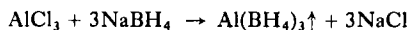
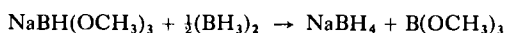


These reactions proceed nicely in diglyme or tetrahydrofuran (8), but these solvents were not available at that time.

A new compound, sodium trimethoxyborohydride, solved the problem.



This compound was very active and achieved the desired reactions without any solvent.



At this time it was reported to us that the problems encountered in the use of uranium hexafluoride had been overcome, so there was no longer any need for other volatile compounds of uranium.

V

ALKALI METAL BOROHYDRIDES

At this point (1943) we were visited by representatives of the Signal Corps. They had learned through our reports that we had a new chemical that might be used for the field generation of hydrogen. They felt that their present method, based on the reaction of alkali with ferrosilicon, was cumbersome and they were seeking a more convenient hydrogen source.

We pointed out that sodium borohydride on a weight basis should be far more efficient than sodium hydroxide and ferrosilicon. Although we had never used it for hydrogen generation, we had no doubt that it would be similar to diborane in reacting readily with water to liberate hydrogen. They asked for a demonstration.

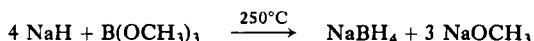
I placed a weighed quantity of sodium borohydride in a flask and attached it to a dropping funnel which contained water. The outlet from the flask was connected to a gas meter. The entire assembly was placed behind an explosion screen, since I did not know how violent the reaction might be.

With Professor Schlesinger and all of the representatives watching me from a safe distance, I cautiously reached behind a screen and turned the stopcock to allow water to flow onto the borohydride.

The borohydride dissolved and the solution sat there merely looking at me!

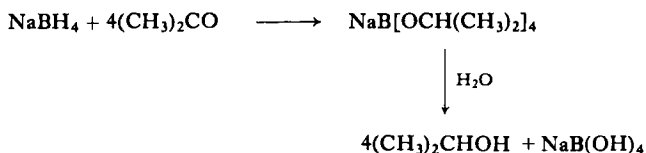
This was one of the great shocks of my life and was the way we discovered that sodium borohydride possesses a remarkable stability (for a simple boron-hydrogen compound) in water.

Fortunately, the Signal Corps was persuaded to support research to find improved methods of preparing sodium borohydride and catalysts to facilitate its solvolysis. We soon discovered that sodium borohydride could readily be prepared by treating sodium hydride with methyl borate at 250° C.



Then we discovered that the addition of 2% of a cobalt salt to pellets of sodium borohydride caused rapid hydrolysis with liberation of hydrogen.

We needed a solvent to separate sodium borohydride from sodium methoxide, concurrently produced in the synthesis. This led to a search for solvents for sodium borohydride. Among the solvents tested was acetone. A vigorous reaction ensued upon addition of the sodium borohydride, the active "hydride" disappeared, and analysis revealed the presence of 4 moles of isopropyl alcohol per mole of sodium borohydride introduced.



In this way we discovered that sodium borohydride was a valuable reagent for the hydrogenation of organic molecules!

Sodium borohydride has been manufactured commercially by this process for many years. It is of interest that a chemical discovered in the course of war research has found its chief application in the manufacture of pharmaceuticals.


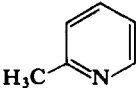
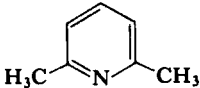
VI

MOLECULAR ADDITION COMPOUNDS AND STERIC STRAINS

At this time, steric effects were in low repute. In the words of a textbook published in 1942 (9), "... steric hindrance is the last refuge of puzzled organic chemists." It appeared that study of the stabilities of addition

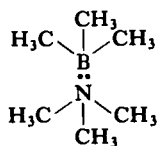
compounds of borane derivatives with amines might provide quantitative data to allow a decision as to the importance of steric effects.

Data, such as those in the tabulation for a group of related pyridine bases, provided convincing evidence (10).

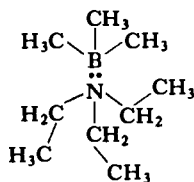
			
pK_a	5.17	5.97	6.75
ΔH , $\text{CH}_3\text{SO}_3\text{H}$	17.1	18.3	19.5
ΔH , $\frac{1}{2}(\text{BH}_3)_2$	20.2	19.7	16.4
ΔH , BF_3	33.3	31.6	25.8
ΔH , BMe_3	21.4	16.1	No reaction

(ΔH in kcal/mole in nitrobenzene solution)

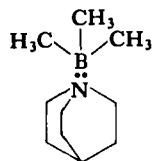
Results with triethylamine and quinuclidine also favored a steric interpretation (11).



$\Delta H = 17.6$



~ 10



20.0

At the present time, steric effects once again play an accepted role in interpretations of organic chemistry (12, 13).

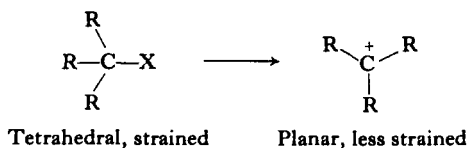
VII

STERIC ASSISTANCE IN SOLVOLYSIS

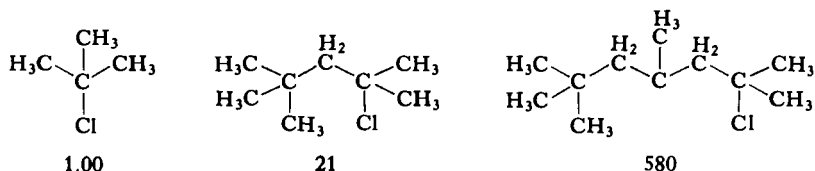
These studies on steric assistance (12) led to a detailed consideration of the possible role of steric effects in a wide variety of systems, such as steric effects in displacement reactions (10, 14), steric effects in elimination reactions (15, 16), steric effects in alicyclic systems (17), and steric effects in

aromatic substitution (18, 19). One area we considered was the role of steric effects in the solvolysis of highly branched tertiary halides (12).

It was suggested that three alkyl groups attached to a central carbon atom would be strained because of steric crowding (20). Such strains would be relieved during ionization to form the less strained planar carbonium ion.



This proposal was tested in a number of systems, such as the following.

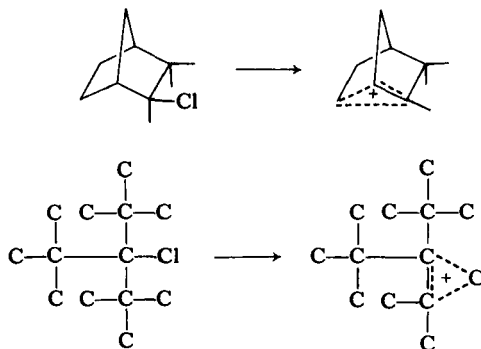


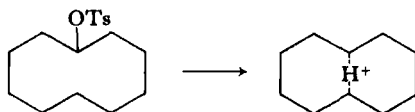
The concept appeared to be widely accepted. Consequently, we left this area for other studies.

VIII

THE NONCLASSICAL ION PROBLEM

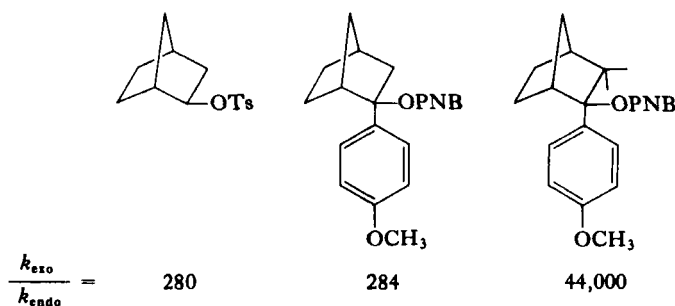
Beginning in 1951, there appeared in the literature an alternative explanation, σ -participation, for enhanced rates of solvolysis of highly branched derivatives (21, 22).





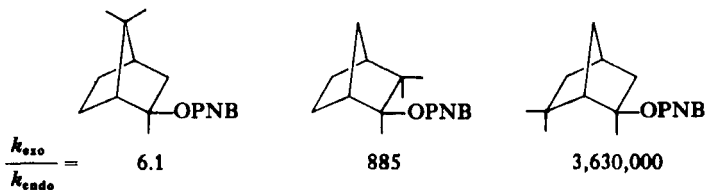
It was puzzling to me that the phenomenon appeared to be important chiefly in strained systems, systems where steric effects could also be involved.

There was general agreement that the norbornyl system provided the best example for such σ -participation leading to the formation of σ -bridged ions. A detailed study of such systems was undertaken. One approach was the synthesis of stabilized tertiary norbornyl derivatives. Such tertiary norbornyl cations must be classical—a stabilized cationic center should not be capable of demanding electronic contributions from the σ -electrons of a carbon-carbon bond. Yet 2-anisylnorbornyl exhibits properties similar to those of the parent norbornyl derivative, such as high exo/endo rate ratio and high exo/endo product ratio (23, 24).



Consequently, these must be the properties of the norbornyl system, rather than a consequence of σ -participation under solvolytic conditions.

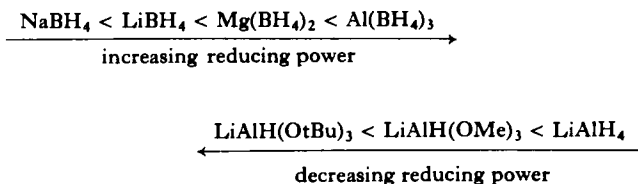
The *gem*-dimethyl substituents in the 3-position of 2-anisylcamphenyl result in a major increase in the exo/endo rate ratio. This can only be a steric phenomenon. The results with the trimethylnorbornyl derivatives supports the importance of steric effects in this rigid system (25, 26).



It is of interest to point out that the original three proposals for enhanced rates due to σ -participation have been withdrawn.

IX SELECTIVE REDUCTIONS

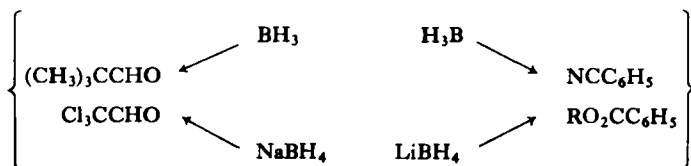
Lithium aluminum hydride is an exceptionally powerful reducing agent, whereas sodium borohydride is a mild one. We undertook to develop a family of reducing agents with capabilities between these extremes (27–30).



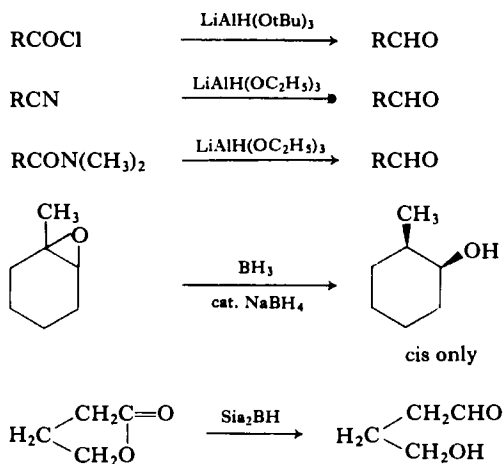
Then we established that borane and its derivatives are “acidic” reducing agents (31–34), in contrast to the “basic” reducing agents, the complex hydrides.

“Basic”	“Acidic”
MBH ₄	BH ₃
MBH(OR) ₃	BHCl ₂
MBHR ₃	BHR ₂
MAIH ₄	AlH ₃
MAIH(OR) ₃	AlHCl ₂
MAIHR ₃	AlHR ₂

We can now do many selective reductions of one group in the presence of a second, or vice versa (28).



Many interesting reductions are now possible, as indicated in the following reactions (28):



The chief difficulty is that of educating chemists to do quantitative work with hydrides and to use the reagent most applicable for the desired transformation.

X

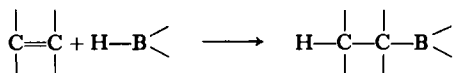
HYDROBORATION

Perhaps the most valuable result of this study (35, 36) of new reducing agents was the discovery of hydroboration. It arose from the following discrepancy (35).

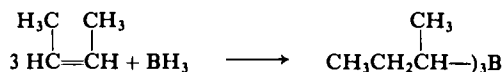
"Hydride" used from AlCl ₃ · 3 NaBH ₄ in diglyme	
Aldehydes	1.0
Ketones	1.0
Acids	2.0 + 1.0 H ₂ ↑
Esters	2.0
Ethyl acetate	2.0
Ethyl stearate	2.0
Ethyl oleate	2.37 ←

Examination of this "anomaly" revealed that the carbon-carbon double bond was also reacting, producing a carbon-boron bond with loss of an equivalent of hydride.

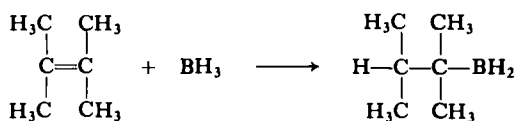
Research soon revealed that diborane in ether solvents reacts readily with olefins (37), acetylenes (38), dienes (39), etc.



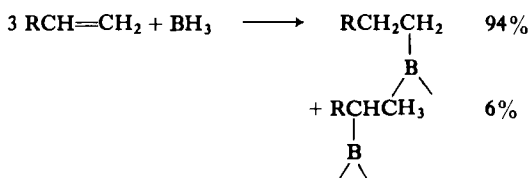
The reaction is quantitative and practically instantaneous (35).



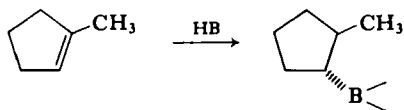
Practically all unsaturated compounds, even highly hindered olefins, react (40).



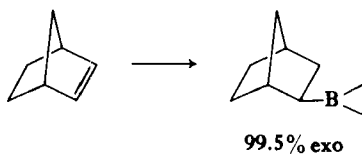
The addition is predominantly anti-Markovnikov (41).



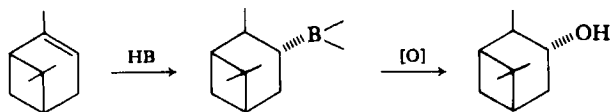
The addition is cis (45).



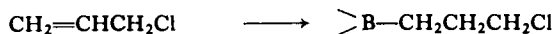
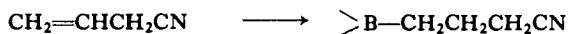
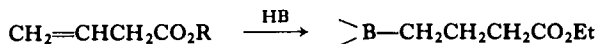
The addition takes place preferentially from the less hindered side of the double bond (42).



No rearrangements of the carbon skeleton have been observed (43).



Many functional groups can tolerate hydroboration (44-46). Thus, for



the first time the organic chemist has readily available organometallics containing functional groups. This promises to have a revolutionary influence upon synthetic procedures in organic chemistry.

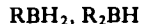
XI

THE VERSATILE ORGANOBORANES

The ready availability of organoboranes next prompted a detailed exploration of their reactions, with emphasis on reactions of utility in synthesis. This exploration proved to be remarkably fruitful—it is clear that the organoboranes are the most versatile organometallic available to the chemist (47, 48).

Even though our program in this area is relatively young, with serious research being initiated only five years ago, the results can no longer be adequately treated in a brief review. Consequently, I can only attempt to indicate the scope of the developments by listing the topics discussed in a recent review (48).

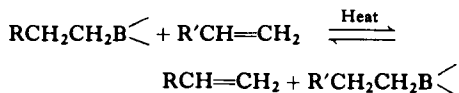
(A) Partially Alkylated Boranes (35, 49)



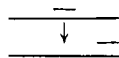
(B) Isomerization (35)



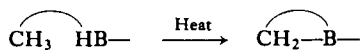
(C) Displacement (35)



(D) Contrathermodynamic Isomerization (35)



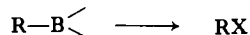
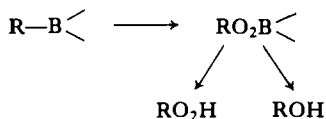
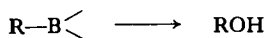
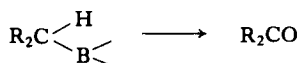
(E) Cyclization (50)



(F) Protonolysis (51)



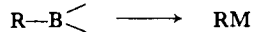
(G) Halogenolysis (52, 53)


 (H) Oxidation (O_2) (54)

 (I) Oxidation (H_2O_2) (35)

 (J) Oxidation (H_2CrO_4) (35)


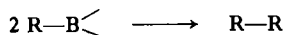
(K) Amination (55)



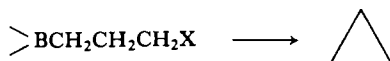
(L) Metalation (56)



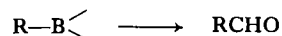
(M) Coupling (57)



(N) Cyclopropane Synthesis (58)



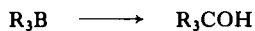
(O) Carbonylation to Aldehydes (59, 60)



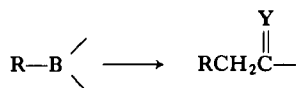
(P) Carbonylation to Ketones (59)



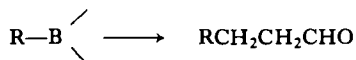
(Q) Carbonylation to Tertiary Alcohols (59)



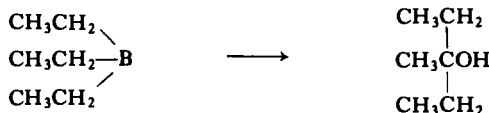
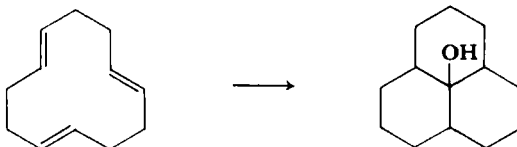
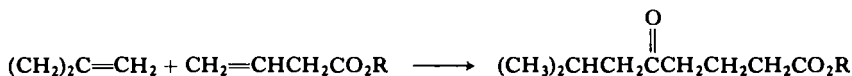
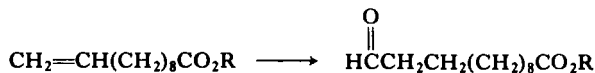
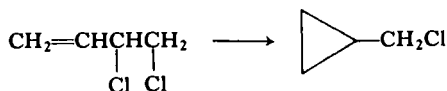
(R) Alkylation and Arylation (61, 62)



(S) Conjugate Additions (63)



The following transformations indicate some of the new possibilities for synthetic work (58, 60, 64-66).



Only a few years have passed since we initiated our systematic survey of the reactions of organoboranes. Optimistic as I was at the time this exploration was initiated, I must admit my own surprise at the immense amount of promising new chemistry that our studies have uncovered.

We have been fully occupied by our explorations. There has been no attempt as yet, in our laboratories or in others', to apply the chemistry to the synthesis of natural products or pharmaceuticals; there has been no attempt to utilize the chemistry for industrial requirements, nor has there yet been any systematic effort to develop the physical organic aspects of this area. All that is still before us. Another major task before us is that of educating students in the experimental methods and techniques of this area of chemistry so that they will not hesitate to apply these fascinating new methods. Clearly we have uncovered a new continent, only partially explored. It will require a major effort on the part of many chemists to continue the exploration and to apply the chemistry for the benefit of mankind.

Finally, I wish to make the point that I was invited to review the results of my own group in this chapter. Many other workers have made important contributions to the organoborane area in recent years. However, progress even within my own group has been so rapid that I could not include all of our own developments in this review. Consequently, I must apologize to other authors for having restricted this chapter primarily to the topics that have occupied the attention of my students and associates. Fortunately, in my recently published Baker Lectures, *Boranes in Organic Chemistry* (Cornell Univ. Press, Ithaca, New York, 1972) it has been possible to provide a fuller, more complete treatment.

XII CONCLUSION

In this review I have traced the experiences of my research associates and myself as we explored the role of boranes in chemistry. Initially diborane was a very rare substance, made in milligram quantities in only a few laboratories throughout the world and explored purely for its scientific interest.

War research forced us to explore new synthetic routes and we discovered the alkali metal hydride route to diborane. This solved the synthetic problem. At the same time we discovered sodium borohydride and developed simple synthetic methods for its preparation and manufacture.

The search for solvents led to the discovery that sodium borohydride is an excellent reducing agent for aldehydes and ketones. The search for catalysts to enhance the reducing power of sodium borohydride led to an anomalous result in the reduction of ethyl oleate. Investigation of this anomalous result led to the discovery of hydroboration.

Hydroboration made the organoboranes readily available for the first time. This led to a systematic exploration of the chemistry of the organoboranes and established the fact that they constitute the most versatile organometallic available presently. A major new area awaits exploration and application.

On the theoretical side, study of the dissociation of addition compounds of amines with trimethylborane, boron trifluoride, and borane provide a new quantitative approach to steric strains. These studies quickly removed doubts as to the importance of steric effects in chemical behavior.

These studies led to the study of related carbon compounds and to the establishment of steric effects as an important factor in their behavior.

One phase of these studies involved steric assistance to ionization in highly branched tertiary halides and related derivatives. This concept was tested and fully supported by a number of studies.

An alternative explanation for the enhanced rates made its appearance. It was proposed that σ -participation in certain nonclassical ions provided a more satisfactory interpretation. This stimulated a detailed study of the norbornyl system, considered to provide the best available case for such nonclassical carbonium ion intermediates. The results failed to confirm the presence of significant σ -participation and supported the conclusion that the phenomena must be largely, if not entirely, steric in origin.

Consequently, these studies of boranes have led us into many areas, both theoretical and practical. There is no evidence that it is any more difficult now than it was 35 years ago to uncover interesting new areas of study. Indeed, our experience indicates the reverse to be true. I can only advise those beginning a research career that it has been my experience that optimism is an essential ingredient of fruitful exploratory research.

In the Introduction I pointed out that I believe we have been doing our students a disservice in divorcing them so severely from knowledge of the past. I hope that this review will contribute to a modification of this situation.

Finally, I wish to acknowledge the major contributions of a remarkable group of students and research associates who have contributed to this program. In a review of this kind, covering fully 35 years of research, it was possible to mention only some of the high spots and to make reference to only a fraction of their publications. I hope I have made amends to the others in my recently published book (67).

REFERENCES

1. Stock, A., "Hydrides of Boron and Silicon." Cornell Univ. Press, Ithaca, New York, 1933.
2. Burg, A. B., and Schlesinger, H. I., *J. Amer. Chem. Soc.* **59**, 780 (1937).
3. Brown, H. C., Schlesinger, H. I., and Burg, A. B., *J. Amer. Chem. Soc.* **61**, 673 (1939).
4. Schlesinger, H. I., Sanderson, R. T., and Burg, A. B., *J. Amer. Chem. Soc.* **62**, 3421 (1940).
5. Schlesinger, H. I., and Burg, A. B., *J. Amer. Chem. Soc.* **62**, 3425 (1940).
6. Schlesinger, H. I., and Burg, A. B., *J. Amer. Chem. Soc.* **53**, 4321 (1931).
7. Schlesinger, H. I., Brown, H. C., *et al.*, *J. Amer. Chem. Soc.* **75**, 186 (1953).

8. Brown, H. C., "The Reactions of Alkali Metal Hydrides and Boro-hydrides with Lewis Acids of Boron and Aluminum," Congr. Lect., 17th Int. Congr. Pure Appl. Chem. p. 167. Butterworths, London, 1960.
9. Ray, F. E., "Organic Chemistry," p. 522. Lippincott, New York, 1941.
10. Brown, H. C., Gintis, D., and Domash, L., *J. Amer. Chem. Soc.* **78**, 5387 (1956).
11. Brown, H. C., and Sujishi, S., *J. Amer. Chem. Soc.* **70**, 2878 (1948).
12. Brown, H. C., *J. Chem. Soc.* 1248 (1956).
13. Brown, H. C., *J. Chem. Educ.* **36**, 424 (1959).
14. Brown, H. C., and Horowitz, R. H., *J. Amer. Chem. Soc.* **77**, 1733 (1955).
15. Brown, H. C., and Moritani, I., *J. Amer. Chem. Soc.* **77**, 3623 (1955).
16. Brown, H. C., and Moritani, I., *J. Amer. Chem. Soc.* **78**, 2203 (1956).
17. Brown, H. C., and Ichikawa, K., *Tetrahedron* **1**, 221 (1957).
18. Nelson, K. L., and Brown, H. C., *J. Amer. Chem. Soc.* **73**, 5605 (1951).
19. Stock, L. M., and Brown, H. C., *Advan. Phys. Org. Chem.* **1**, 35 (1963).
20. Brown, H. C., *Science* **103**, 385 (1946).
21. Brown, H. C., *Chem. Brit.* **2**, 199 (1966).
22. Brown, H. C., *Chem. Eng. News* **45**, No. 7, 87 (1967).
23. Brown, H. C., and Takeuchi, K., *J. Amer. Chem. Soc.* **90**, 2691 (1968).
24. Brown, H. C., and Takeuchi, K., *J. Amer. Chem. Soc.* **90**, 5268 (1968).
25. Brown, H. C., and Ikegami, K., *J. Amer. Chem. Soc.* **90**, 7122 (1968).
26. Ikegami, S., Vander Jagt, D. L., and Brown, H. C., *J. Amer. Chem. Soc.* **90**, 7124 (1968).
27. Brown, H. C., *J. Chem. Educ.* **38**, 173 (1961).
28. Brown, H. C., *Atti Accad. Naz. Lincei* **31** (1968).
29. Brown, H. C., and Subba Rao, B. C., *J. Amer. Chem. Soc.* **78**, 2582 (1956).
30. Brown, H. C., and McFarlin, R. F., *J. Amer. Chem. Soc.* **80**, 5372 (1958).
31. Brown, H. C., and Subba Rao, B. C., *J. Amer. Chem. Soc.* **82**, 681 (1960).
32. Brown, H. C., Heim, P., and Yoon, N. M., *J. Amer. Chem. Soc.* **92**, 1637 (1970).
33. Brown, H. C., Bigley, D. B., Arora, S. K., and Yoon, N. M., *J. Amer. Chem. Soc.* **92**, 7161 (1970).
34. Yoon, N. M., and Brown, H. C., *J. Amer. Chem. Soc.* **90**, 2927 (1968).
35. Brown, H. C., "Hydroboration." Benjamin, New York, 1962.
36. Brown, H. C., *Atti Accad. Naz. Lincei* **51** (1968).
37. Brown, H. C., and Subba Rao, B. C., *J. Org. Chem.* **22**, 1136 (1957).
38. Brown, H. C., and Zweifel, G., *J. Amer. Chem. Soc.* **81**, 1512 (1959).
39. Brown, H. C., and Zweifel, G., *J. Amer. Chem. Soc.* **81**, 5832 (1959).
40. Brown, H. C., and Moerikofer, A. W., *J. Amer. Chem. Soc.* **84**, 1478 (1962).
41. Brown, H. C., and Zweifel, G., *J. Amer. Chem. Soc.* **82**, 4708 (1960).
42. Brown, H. C., and Zweifel, G., *J. Amer. Chem. Soc.* **83**, 2544 (1961).
43. Zweifel, G., and Brown, H. C., *J. Amer. Chem. Soc.* **86**, 393 (1964).
44. Brown, H. C., and Unni, M. K., *J. Amer. Chem. Soc.* **90**, 2902 (1968).
45. Brown, H. C., and Gallivan, P. M., *J. Amer. Chem. Soc.* **90**, 2906 (1968).
46. Brown, H. C., and Sharp, R. L., *J. Amer. Chem. Soc.* **90**, 2915 (1968).
47. Brown, H. C., *Atti Accad. Naz. Lincei* **73** (1968).
48. Brown, H. C., *Chem. Brit.* **7**, 458 (1971).
49. Knights, E. F., and Brown, H. C., *J. Amer. Chem. Soc.* **90**, 5280, 5281 (1968).
50. Brown, H. C., Murray, K. J., Müller, H., and Zweifel, G., *J. Amer. Chem. Soc.* **88**, 1443 (1966).
51. Brown, H. C., and Murray, K., *J. Amer. Chem. Soc.* **81**, 4108 (1959).
52. Brown, H. C., Rathke, M. W., and Rogić, M. M., *J. Amer. Chem. Soc.* **90**, 5038 (1968).

53. Brown, H. C., and Lane, C. F., *J. Amer. Chem. Soc.* **92**, 6660 (1970).
54. Brown, H. C., Midland, M. M., and Kabalka, G. W., *J. Amer. Chem. Soc.* **93**, 1024 (1971).
55. Brown, H. C., Heydkamp, W. R., Breuer, E., and Murphy, W. S., *J. Amer. Chem. Soc.* **86**, 3565 (1964).
56. Larock, R. C., and Brown, H. C., *J. Amer. Chem. Soc.* **92**, 2467 (1970).
57. Brown, H. C., Hébert, N. C., and Snyder, C. H., *J. Amer. Chem. Soc.* **83**, 1001 (1961).
58. Brown, H. C., and Rhodes, S. P., *J. Amer. Chem. Soc.* **91**, 2149, 4306 (1969).
59. Brown, H. C., *Accounts Chem. Res.* **2**, 65 (1969).
60. Brown, H. C., and Coleman, R. A., *J. Amer. Chem. Soc.* **91**, 4606 (1969).
61. Brown, H. C., Rogić, M. M., Rathke, M. W., and Kabalka, G. W., *J. Amer. Chem. Soc.* **90**, 818, 1911, 6218 (1968).
62. Brown, H. C., and Rogić, M. M., *J. Amer. Chem. Soc.* **91**, 2146 (1969).
63. Suzuki, A., Arase, A., Matsumoto, H., Itoh, M., Brown, H. C., Rogić, M. M., and Rathke, M. W., *J. Amer. Chem. Soc.* **89**, 5708 (1967).
64. Brown, H. C., and Negishi, E., *J. Amer. Chem. Soc.* **89**, 5285 (1967).
65. Brown, H. C., and Negishi, E., *J. Amer. Chem. Soc.* **89**, 5478 (1967).
66. Lane, C. F., and Brown, H. C., *J. Amer. Chem. Soc.* **93**, 1025 (1971).
67. Brown, H. C., "Boranes in Organic Chemistry." Cornell Univ. Press, Ithaca, New York, 1972.

Transition Metal–Isocyanide Complexes

PAUL M. TREICHEL

*Department of Chemistry
University of Wisconsin
Madison, Wisconsin*

I. Introduction	21
II. Structure and Bonding	23
III. Current Topics	28
A. Insertion Reactions into Metal–Carbon Bonds	28
B. Nucleophilic Reactions with Metal Isocyanide Complexes	36
C. Additions of Protonic Compounds to Coordinated Isocyanides	42
D. Copper-Catalyzed α -Additions to Isocyanide	47
IV. Isocyanide Complexes of Various Metals	49
A. Group VIB	49
B. Group VIIB	54
C. Iron, Ruthenium, Osmium	58
D. Cobalt, Rhodium, Iridium	63
E. Nickel, Palladium, Platinum	68
F. Other Metals	80
References	81

I

INTRODUCTION

The field of transition metal complexes of isocyanides developed slowly over more than a century to a respectable subarea in coordination chemistry, and in the process seems to have attracted very little attention. Even the remarkable resurgence of transition metal organometallic chemistry in the last 20 years, and the realization that isocyanides and carbon monoxide should be quite similar as ligand groups in organometallic complexes, did not initiate an extensive development of this area of chemistry. Only in the last several years has this potentially important subject begun to receive the attention it would seem to deserve.

No doubt, the publication of an excellent monograph several years ago has caused some attention to be focused on this subject. Malatesta and Bonati (90) have carefully reviewed the subject of isocyanide–transition metal

complex chemistry from its early origins with the alkylations of metal cyanides to more recent studies on ligand reactions. Because this monograph provides an adequate review of this field up to about 1967, an extensive historical and background review is not necessary here and will not be presented. Instead, this article will concentrate on work which has evolved since that date; this, needless to say, is substantial due to the rapid evolution of this field.

While on the subject of reviews, attention should also be directed to a very recent collection of articles on isocyanide chemistry edited by Ugi (156). This volume is oriented somewhat toward the organic chemistry of isocyanides, but not with the complete exclusion of metal complexes of these species; one is directed in particular to the chapters by Vogler (Chapter 10) on coordinated isocyanides and by Saegusa and Ito (Chapter 4) on α -additions to isocyanides. These latter reactions are often catalyzed by copper(I) compounds and occasionally by other metal complexes as well, and it is believed that this catalysis is accomplished by intermediate formation of metal isocyanide complexes.

There is a 1968 review of metal isocyanide complexes in Japanese (122); this is not generally accessible, however.

The subjects of structure and bonding in metal isocyanide complexes have been discussed before (90, 156) and will not be treated extensively here. A brief discussion of this subject is presented in Section II; of course, special emphasis is given to the more recent information which has appeared. Several areas of current study in the field of transition metal-isocyanide complexes have become particularly important and are discussed in this review in Section III. These include the additions of protonic compounds to coordinated isocyanides, probably the subject most actively being studied at this time; insertion reactions into metal-carbon bonded species; nucleophilic reactions with metal isocyanide complexes; and the metal-catalyzed α -addition reactions. Concurrent with these new developments, there has been a general expansion of descriptive chemistry of isocyanide-metal complexes, and further study of the physical properties of selected species. These developments are summarized in Section IV.

Common abbreviations are used in this article, and are defined below.

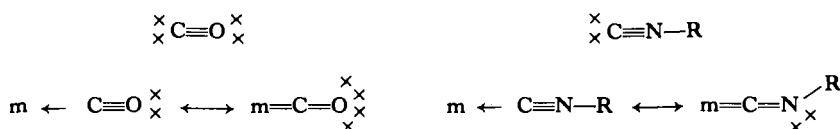
CNR	An alkyl (or cycloalkyl) isocyanide
CNAr	An aryl isocyanide
Me	Methyl

Et	Ethyl
Cy	Cyclohexyl
Ph	Phenyl
Bu	Butyl
Bu'	<i>tert</i> -Butyl
tol	<i>p</i> -Tolyl
phos	Phosphines, PR ₃
L	Ligand (unspecified)
diphos	1,2-Bis(diphenylphosphino)ethane
M	Metal (unspecified)

II

STRUCTURE AND BONDING

The valence-bond pictures for an isocyanide and carbon monoxide, and for metal complexes of these ligands, emphasize the similarities of both the ligands and their complexes.



The metal–ligand bonding can be viewed as the sum of a σ -bond, involving donation of the lone pair of electrons on carbon to the metal, and a π -bond, in which metal electrons are transferred to π^* (π_{CO}^* or π_{CN}^*) antibonding orbitals on the ligand. The σ - and π -bonds reinforce each other; the net effect is a multiple metal–carbon linkage; and at the same time a lowering of the carbon–oxygen or carbon–nitrogen bond order is predicted, the magnitude being related to the extent of the π -contribution to bonding.

This simple picture of bonding is convenient to use, and often completely acceptable. However, it does lack sophistication and may not be used to explain some of the subtleties of these systems. One obvious point in this regard concerns infrared spectral data. Coordination of carbon monoxide to a metal invariably leads to a lower carbonyl stretching frequency (ν_{CO}), implying a lower CO bond order as predicted. However, the values for ν_{CN} may be considerably higher for metal complexes of an isocyanide than are the values for the ligand itself. The valence-bond picture cannot rationalize

an increase in ν_{CN} . There is also the weight of a considerable amount of descriptive chemistry to suggest that carbon monoxide and isocyanides must be substantially different as ligands. Thus, metal-isocyanide complexes with the metal in a low-valent (0, -1) state are quite uncommon, in contrast to the wide variety of carbonyl complexes known; whereas isocyanide complexes of metals with higher valencies (+1, +2) are reasonably common in comparison to analogous carbonyl species. The implication here is that carbon monoxide is better able to stabilize low-valent complexes than are isocyanides; however, one hastens to note that "ability to stabilize" is not adequately defined either here or elsewhere.

The valence-bond picture does not adequately express a difference between various isocyanides. There are interesting differences between alkyl and aryl isocyanides, discussed below.

Generally, ν_{CN} is shifted to higher frequencies in metal isocyanide complexes in higher oxidation states, and to lower frequencies for low-valent systems. This observation is in accord with the valence-bond picture. For the higher-valent species σ -bonding from ligand to metal predominates. The π -bonding becomes increasingly important in the low-valent systems where the negative charge on the metal is greater; with increased π -bonding a shift of ν_{CN} to lower frequency is expected.

Incidentally, isocyanides are polar (for CNC_6H_5 the dipole moment is 3.44 D) and they are good bases (vs. BR_3 , H^+), whereas CO is a poor base; hence isocyanides can function as ligands in metal complexes where carbon monoxide does not. The scarcity of low-valent isocyanide complexes is less easily explained, however. Arguments involving π -acceptor capacity are quite inappropriate. More data on low-valent species, and evaluations of stabilities, modes of decomposition, and reactions are desirable.

A simple molecular orbital picture (using, e.g., an ML_6^{+n} species for convenience) may be constructed by first looking at the appropriate ligand (CO or CNR) orbitals, i.e., the carbon lone pair and the π_{CO}^* or π_{CN}^* orbitals, and then evaluating the appropriate metal-ligand bonding. The paper by Caulton and Fenske (35) on metal carbonyl bonding provides a good basis for this discussion.

Caulton and Fenske began with a molecular orbital diagram for CO (see Fig. 1). The two orbitals of interest here are, of course, the 5σ - and 2π -orbitals. The 5σ -orbital, assumed in valence-bond theory to be a carbon orbital, has in reality a small contribution from oxygen also ($5\sigma = 0.664 2s^c + 0.059 2s^o - 0.664 2p^c - 0.364 2p^o$). One can see from the choice of

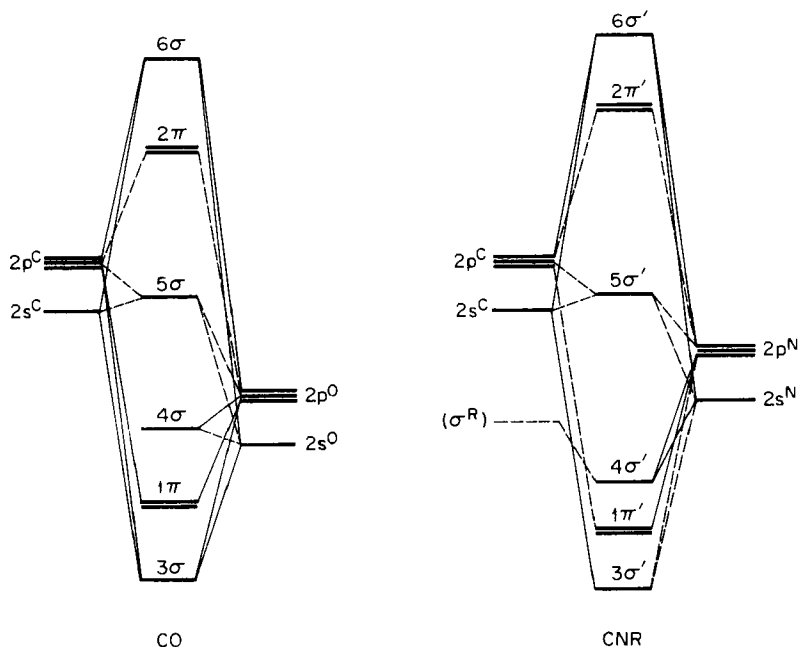


FIG. 1. MO descriptions for CO and CNR (not to scale). CO: $(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^4(4\sigma)^2(5\sigma)^2$; CNR: $(1\sigma')^2(2\sigma')^2(3\sigma')^2(1\pi')^4(4\sigma')^2(5\sigma')^2$. From Caulton and Fenske (35).

coefficients that this orbital is somewhat antibonding with respect to carbon and oxygen. In bonding to a metal, if electrons are donated from this orbital to the metal, the carbon–oxygen antibonding contribution will be decreased and the CO bond order and the CO frequency raised accordingly. At the same time π -bonding, involving delocalization of electrons into the 2π (π^*) ligand orbitals, would decrease the CO bond order and also ν_{CO} . Thus σ - and π -bonding have opposite effects on the CO bond order and CO stretching frequency. In low-valent metal carbonyl species, the metal–ligand π -bonding is substantial and the shift of ν_{CO} to lower frequencies is anticipated and observed.

The same model could be applied to metal isocyanide complexes. For the isocyanide ligand one can propose an orbital diagram similar to CO (Fig. 1) except that 4σ in the CO system is now a bonding orbital between nitrogen and the R group. The orbitals to be used in bonding to a metal are $5\sigma'$ and $2\pi'$. Lacking calculations, it is difficult to compare energies for those orbitals with energies of 5σ and 2π . However, knowing something of the results

expected, one might predict both $5\sigma'$ and $2\pi'$ to be at higher energy than 5σ and 2π for a carbonyl. This would make the isocyanide a better donor and a poorer acceptor than CO.

Note that this picture would have to be adapted still further to take into account the nature of the R group in RNC.

Finally, one might approach the bonding in an $M(\text{CNR})_6^{n+}$ complex in a different fashion, by looking first at $M(\text{CN})_6^{n-6}$, and evaluating the effect of adding six R^+ groups to the system (133).

Coordination to an isocyanide can either raise or lower the value of ν_{CN} depending on the relative contributions of σ - and π -bonding. These contributions are dependent on metal orbital energies, which are influenced by oxidation state and by other ligands present.

One might observe in passing that the valence-bond picture for isocyanide-metal bonding suggests that with increasing π -donation to the ligand the C—N—C angle will decrease from 180° . This appears not to be commonly observed; in those complexes whose structures are known an approximately linear arrangement of atoms is found. In explanation, one can observe that this nonlinearity will result only if π -bonding would occur preferentially to one of the two degenerate π^* -orbitals. Equivalent retrodonative π -bonding to both π^* -orbitals would be cylindrically symmetric and would not be expected to have any effect on this geometry.

One additional point should be discussed here, concerning the substantial emphasis that has been placed on the differences between alkyl and aryl isocyanides. It has been suggested, primarily on the basis of infrared evidence, that aryl isocyanides are better π -acceptors than alkyl isocyanides (90). Qualitatively this difference is easily rationalized. One can see that delocalization of charge into π^* -orbitals on an aryl ring in aryl isocyanide-metal complexes should be possible, whereas no such possibility exists for alkyl isocyanide-metal complexes; this means that aryl isocyanides should be better π -acceptors. Of course, the simple qualitative model gives one no measure of the relative importance of this effect.

The infrared evidence bearing on this conclusion is reviewed by Malatesta and Bonati (90), and need not be presented here in detail. It is observed only that comparisons are made between the values of ν_{CO} (or CO force constants) for series of analogous compounds such as $\text{Ni}(\text{CO})_{4-x}\text{L}_x$ or $\text{M}(\text{CO})_{6-x}\text{L}_x$ ($M = \text{Cr}, \text{Mo}, \text{W}$; $L = \text{CNR}, \text{CNAr}, \text{phos}, \text{etc.}$); also comparisons are often made between the values of ν_{CN} for the free ligand and for the ligand bonded in a metal complex. Much of this work dates back over

ten years, and the interpretations made tend to overemphasize π -bonding of the ligand and ignore any differences in σ -bonding. The use of π -bonding only in the interpretation of infrared data is not currently acceptable. In addition it is important to observe that the difference in ν_{CO} , or in $\Delta\nu_{\text{CN}}$ for analogous complexes, is not generally large, so there is some question of the importance of this effect.

More important than this, however, is the fact that until recently there have been no substantial differences observed in the chemistry of metal complexes of alkyl and aryl isocyanides. In general, the choice of which isocyanide to use seems to be made largely at random, dictated perhaps by convenience as much as any other factor. Lacking any substantial chemical differences between the two groups of complexes, one might wish to minimize, rather than emphasize, this comparison. However, several observations have recently been made which seem to substantiate the earlier conclusion.

Of particular interest is an electrochemistry study on related $\text{Mn}(\text{CNR})_6^+$ complexes, and on several carbonyl species (154). The one-electron oxidation process in acetonitrile ($\text{Mn}(\text{CNR})_6^+ \rightarrow \text{Mn}(\text{CNR})_6^{2+}$) is substantially

TABLE I
CYCLIC VOLTAMMETRIC DATA ON MANGANESE(I)
ISOCYANIDE SPECIES^{a, b}

Compound	+1 \rightarrow +2	+2 \rightarrow +3
$[\text{Mn}(\text{CNCH}_3)_6]\text{PF}_6$	0.38	1.54
$[\text{Mn}(\text{CNC}_6\text{H}_4\text{OCH}_3)_6]\text{PF}_6$	0.69	1.55
$[\text{Mn}(\text{CNC}_6\text{H}_4\text{CH}_3)_6]\text{PF}_6$	0.76	1.69
$[\text{Mn}(\text{CNC}_6\text{H}_5)_6]\text{PF}_6$	0.83	1.77
$[\text{Mn}(\text{CNC}_6\text{H}_4\text{Cl})_6]\text{PF}_6$	0.89	1.79
$[\text{Mn}(\text{CO})(\text{CNCH}_3)_5]\text{PF}_6$	0.79	1.99
$[\text{Mn}(\text{CO})(\text{CNC}_6\text{H}_5)_5]\text{PF}_6$	1.11	2.15 ^d
$[\text{Mn}(\text{CO})_2(\text{CNCH}_3)_4]\text{PF}_6$	1.12	
$[\text{Mn}(\text{CO})_3(\text{CNCH}_3)_3]\text{PF}_6$	1.65	
$[\text{Mn}(\text{CO})_4(\text{CNCH}_3)_2]\text{PF}_6$	2.14 ^c	
$[\text{Mn}(\text{CO})_5(\text{CNCH}_3)]\text{PF}_6$	2.65 ^d	

^a From ref. (154).

^b One-half the sum of the cathodic and anodic peaks, in volts, vs. saturated calomel electrode (KCl).

^c Anodic peak not well defined.

^d Value of the cathodic peak; anodic peak not defined.

easier for the methyl isocyanide complex than for analogous aryl isocyanide complexes; $E_{1/2}$ for the former process is 0.38 V vs. 0.83 V for the latter (Table I). Among the various substituted phenyl isocyanide complexes there was a smaller, though still substantial, difference. It would be attractive to relate the ease of oxidation to the electron-withdrawing ability of the ligand in the reactant alone, a higher positive charge on the metal making oxidation more difficult. However, this conclusion is not justified, as the ease of oxidation must involve an energy difference between reactant and product.

Still, the ease of oxidation is obviously a property of considerable chemical importance. These differences require that the choice of aryl vs. alkyl isocyanides not be taken lightly.

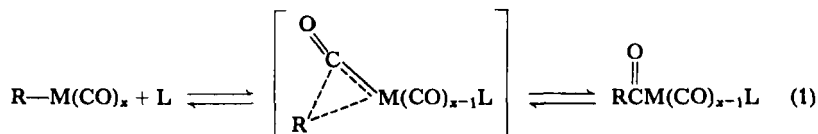
There are a few instances where there may be other chemical differences. For example, it has not yet been possible to prepare $\text{Cr}(\text{CNCH}_3)_6$ by the standard route, nor is it possible to prepare $\text{C}_5\text{H}_5\text{Mn}(\text{CNCH}_3)_3$ from NaC_5H_5 and $\text{Mn}(\text{CNCH}_3)_6^+$, although the analogous phenyl isocyanide complex is formed in this type of reaction (112). One is tempted to attribute the failures to synthesize these low-valent species to the poorer electron-withdrawing ability of CH_3NC ; but, of course, such a conclusion, based on limited evidence (and on the nonexistence of these compounds) is premature at best, and perhaps unwarranted. The results do suggest a current challenge to chemists involved in synthesis, however.

III

CURRENT TOPICS

A. Insertion Reactions into Metal-Carbon Bonds

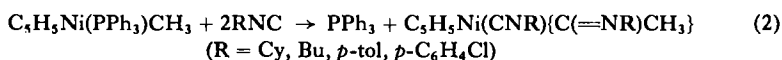
The insertion of a carbonyl group into a metal-alkyl or metal-aryl bond, and the reverse reaction involving decarbonylation of an acyl complex, have been studied from both the synthetic and mechanistic points of view. The mechanism proposed for this type of reaction seems well established and is



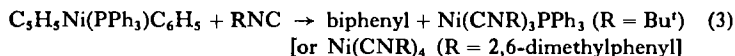
quite general [Eq. (1)]. This reaction has practical consequences; for example, it is believed to play a key role in the oxo (hydroformylation) process.

It seems reasonable to expect that analogous reactions will occur with isocyanide-metal alkyl and aryl complexes. Migration of the organic group to the isocyanide would yield acylimino metal compounds. Such species, formally viewed as derivatives of ketonic (or acyl) complexes, would not be new, but most certainly are not very common, at least up to this time. Isolable acylimino-metal complexes have been reported from four distinct types of reactions. The isocyanide insertion reactions, discussed here, are one general route. A second route involves nucleophilic attack of organolithium species on certain cationic metal isocyanide complexes (Section III,B). Third, the reaction of $C_5H_5Fe(CO)_2CH_3$ and CF_3CN is reported to give $C_5H_5Fe(CO)(CF_3CN)C(=NH)CF_3$; and several derivatives of this complex are obtained by carbonyl substitution (83). Finally, there is a very recent report (84a) that rhodium (I) complexes will undergo oxidative addition reactions with compounds $RC(=NR')Cl$ to give acylimino complexes.

The work on insertion reactions of isocyanides was initiated by Yamamoto *et al.*, and described in a communication in 1968 followed by a full paper a year later (164). This study described the reaction of $C_5H_5Ni(PPh_3)CH_3$ with several isocyanides, from which the products $C_5H_5Ni(CNR)\{C(=NR)CH_3\}$ were isolated [Eq. (2)].



Presumably this reaction proceeds via substitution of phosphine by isocyanide, followed by migration of the alkyl group and addition of the second isocyanide. The intermediate was not isolated, however. Though thermally stable, these nickel complexes are moisture-sensitive, hydrolysis occurring with degradation of the complex and isolation of an amide. For example, from the product above (R = Cy), *N*-cyclohexylacetamide was obtained. It is interesting to observe that this insertion reaction could not be extended to the analogous nickel-phenyl compound $C_5H_5Ni(PPh_3)C_6H_5$. Reactions of this species with various isocyanides led instead to reduction [Eq. (3)].



Surprisingly, no reaction occurred between $C_5H_5Ni(PPh_3)C_6H_5$ and mesityl isocyanide, a result which the authors attribute to steric effects.

The reason for the striking difference between methyl- and phenyl-nickel complexes is not obvious at this time. It does serve notice, however, that generalizations about these reactions may be tenuous at best, and suggests that ample evidence be accumulated before making any generalizations.

Although $C_5H_5Ni(PR_3)\{C(=NR)C_6H_5\}$ complexes are unobtainable by the insertion reaction above, they can be prepared by nucleophilic attack of C_6H_5Li on $[C_5H_5Ni(PR_3)(CNC_6H_{11})]^+$ ($R = Ph, Et$).

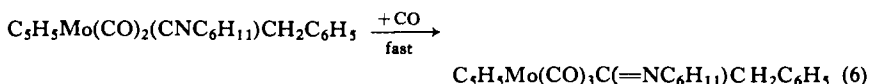
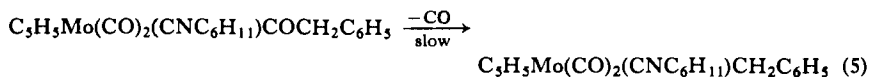
Yamamoto and Yamazaki (166, 167) have also carried out similar reactions with $C_5H_5Mo(CO)_3R$ complexes ($R = CH_3, CH_2C_6H_5$; no reaction when $R = CH_2Cl$ or CH_2CN). In reactions of both the methyl and benzyl complex with several isocyanides ($R'NC = \textit{tert}$ -butyl and 2,6-dimethylphenyl isocyanide) only a single product type was found (166). This had the formula $C_5H_5Mo(CO)_2(CNR')COR$ ($R = CH_3$ and $CH_2C_6H_5$); these complexes have a trans geometry in the solid state, but appear to be a cis-trans mixture in solution. The reaction to give these products is analogous to reactions of other ligands with alkyl and aryl complexes of this formulation. The benzyl complex, $C_5H_5Mo(CO)_2(CNR')COCH_2C_6H_5$, decarbonylates on ultra-violet irradiation to give $C_5H_5Mo(CO)_2(CNR')CH_2C_6H_5$, also an anticipated reaction.

Further reactions of $C_5H_5Mo(CO)_3CH_2C_6H_5$, and of para-substituted benzyl metal complexes, and $C_6H_{11}NC$ were not so straightforward, however (167). Two products were obtained, the first analogous to that described above, the second having the formulation $C_5H_5Mo(CO)_3\{C(=NC_6H_{11})CH_2C_6H_5\}$. This latter complex exists as two isomers, arising due to the orientation of the R group, cis or trans to $CH_2C_6H_5$, with respect to the carbon-nitrogen double bond. Interestingly, the percentage of this compound relative to $C_5H_5Mo(CO)_2(CNC_6H_{11})COCH_2C_6H_5$ increases with increasing electron-attracting power of the para-substituent on the benzyl group.

The formation of the acylimino complexes in these reactions remains something of a puzzle. The quite attractive possibility that direct migration of the benzyl group from CO to CNR occurs cannot be supported since $C_5H_5Mo(CO)_2(CNC_6H_{11})COCH_2C_6H_5$ cannot be converted to $C_5H_5Mo(CO)_3\{C(=NC_6H_{11})CH_2C_6H_5\}$ [Eq. (4)]. Yamamoto and Yama-



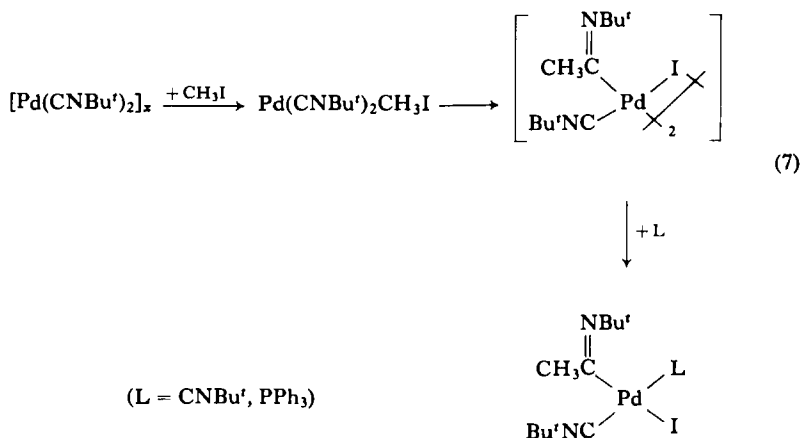
zaki suggest a direct insertion reaction, but such a reaction has no known precedent in carbonyl chemistry. The most likely alternative would involve a two-step conversion [Eqs. (5, 6)]. This suggestion could be checked



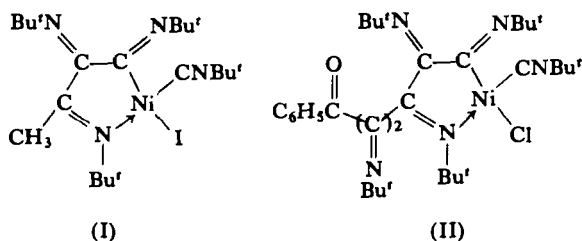
relatively easily. The decarbonylation reaction is known to occur (166) (in one instance) but the second reaction has yet to be studied.

Yamamoto and Yamazaki also suggest that the higher steric requirements of *tert*-butyl and 2,6-dimethylphenyl isocyanides determine the lack of an acylimino-nickel complex in their reactions with $\text{C}_5\text{H}_5\text{Ni}(\text{PPh}_3)\text{CH}_3$ (166).

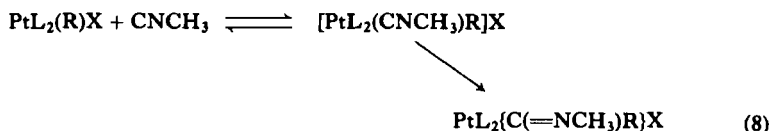
Substantially more work has been done on reactions of square-planar nickel, palladium, and platinum alkyl and aryl complexes with isocyanides. A communication by Otsuka *et al.* (108) described the initial work in this area. These workers carried out oxidative addition reactions with $\text{Ni}(\text{CNBu}^t)_4$ and with $[\text{Pd}(\text{CNBu}^t)_2]_x$. In a reaction of the latter compound with methyl iodide the complex, $\text{Pd}(\text{CNBu}^t)_2(\text{CH}_3)\text{I}$, stable as a solid but unstable in solution, was obtained. This complex when dissolved in toluene proceeds through an intermediate believed to be dimeric, which then reacts with an additional ligand L (CNBu^t or PPh_3) to give $\text{PdL}(\text{CNBu}^t)\text{-}\{\text{C}(\text{CH}_3)=\text{NBu}^t\}\text{I}$ [Eq. (7)].



In the reaction of $\text{Ni}(\text{CNBu}^t)_4$ and methyl iodide oligomerization of the isocyanide was observed; the only isolable nickel complex was (I), shown below. This product is believed to arise through sequential insertions of three isocyanides into a nickel-carbon bond. Upon further treatment with additional isocyanide at a temperature greater than 60°C one obtains a polymer $(\text{RNC})_x$, presumably through multiple isocyanide insertion reactions. The addition of benzoyl chloride to $\text{Ni}(\text{CNBu}^t)_4$ gave two isolable compounds $\text{Ni}(\text{CNBu}^t)_3(\text{COPh})\text{Cl}$ (74%) and (II) (8.2%). This latter reaction, and the isolation of (II) in particular, suggests that the proposed mechanism for polymerization of isocyanides is reasonable.



Reactions of $\text{Pt}(\text{PPh}_3)_2(\text{R})\text{X}$ ($\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) and methyl isocyanide (144) and analogous reactions of $\text{Pd}(\text{phos})_2(\text{CH}_3)\text{I}$ ($\text{phos} = \text{PPh}_3, \text{PPhMe}_2$) complexes with cyclohexyl isocyanide (169, 170) were reported about the same time. As might perhaps be anticipated, the platinum reactions were slower and one can isolate the intermediate species and observe their rearrangement to the inserted products [Eq. (8)]. The isolation of the



($\text{L} = \text{PPh}_3$;

$\text{R} = \text{CH}_3, \text{X} = \text{Br}, \text{I}$;

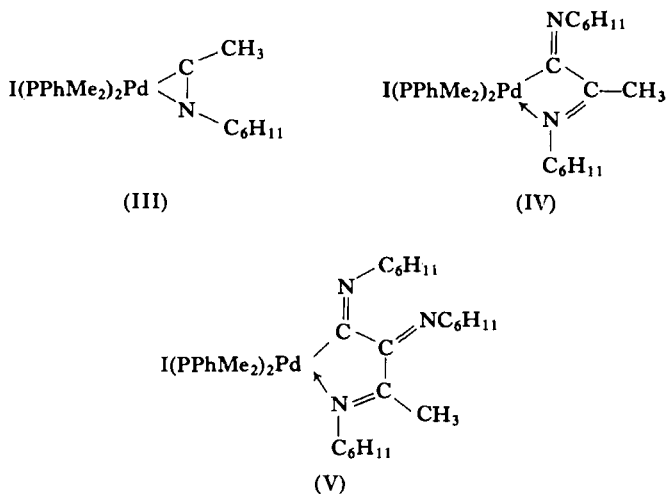
$\text{R} = \text{C}_6\text{H}_5, \text{X} = \text{Cl}, \text{Br}, \text{I}$)

ionic product, as a reaction intermediate, was quite remarkable in that few reactions of this general type give isolable products; rather an equilibrium favoring the reactants seems to be the general rule. However, this pattern of reactivity for isocyanides $\text{Pt}(\text{phos})_2\text{RX} + \text{RNC} \rightarrow [\text{Pt}(\text{phos})_2(\text{CNR})\text{X}]\text{X}$ seems quite general, with several other examples having now been cited (147).

It is interesting to observe that the product in the above reaction sequence will add another isocyanide ligand to give $[\text{Pt}(\text{PPh}_3)_2(\text{CNCH}_3)\text{-}\{\text{C}(=\text{NCH}_3)\text{R}\}]\text{X}$ but that this product does not further rearrange, at least under the relatively mild reaction conditions used (144).

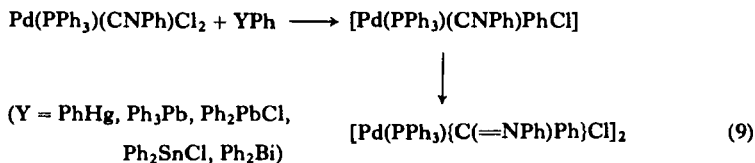
This work (144) failed in an attempt to extend this insertion reaction to the complex $\text{Pt}(\text{PPh}_3)_2(\text{C}_6\text{F}_5)\text{Br}$; a weak 1:1 adduct with CNCH_3 was observed, which rearranged on reflux in benzene with dealkylation of the isocyanide giving $\text{Pt}(\text{phos})_2(\text{C}_6\text{F}_5)\text{CN}$ (145). The failure of the insertion reaction to occur is perhaps not surprising though; insertion reactions of any sort have yet to be accomplished with fluorocarbon-metal complexes.

The addition of cyclohexyl isocyanide to several palladium(II) methyl complexes has proven particularly interesting (169, 170). From $\text{Pd}(\text{PPh}_3)_2\text{CH}_3\text{I}$ the products $\text{Pd}(\text{PPh}_3)_2\{\text{C}(=\text{NC}_6\text{H}_{11})\text{CH}_3\}\text{I}$ (III) and $\text{Pd}(\text{PPh}_3)_2\{(\text{C}=\text{NC}_6\text{H}_{11})_2\text{CH}_3\}\text{I}$ (IV) are obtained, using isocyanide:palladium ratios of 1:1 and 2:1, respectively. The latter complex is, of course, the product resulting from insertion of two isocyanide groups into the metal-carbon bond; however, the former compound is *not* converted to the latter with excess isocyanide, so the origin of the latter appears somewhat of a mystery. Reacting *trans*- $\text{Pd}(\text{PPhMe}_2)_2(\text{CH}_3)\text{I}$ and $\text{CNC}_6\text{H}_{11}$ in benzene at 0°C further compounds the problem as only the product $\text{Pd}(\text{PPhMe}_2)_2\{(\text{C}=\text{NC}_6\text{H}_{11})_2\text{CH}_3\}\text{I}$ is obtained initially, but this may then be converted by excess isocyanide to $\text{Pd}(\text{PPhMe}_2)_2\{(\text{C}=\text{NC}_6\text{H}_{11})_3\text{CH}_3\}\text{I}$, (V) by yet an additional isocyanide insertion.



One remarkable observation was made by Yamamoto and Yamazaki in this work (170); this was that for both the single and double insertion products, (III) and (IV), from $\text{Pd}(\text{PPhMe}_2)_2(\text{CH}_3)\text{I}$ the two phosphine methyl groups are dissimilar. Thus, in the PMR spectrum for $\text{Pd}(\text{PPhMe}_2)_2\{\text{C}(=\text{NC}_6\text{H}_{11})\text{CH}_3\}\text{I}$ at 23°C the methyl groups give a 1:2:2:2:1 pattern, the result of the partial overlap of two 1:2:1 triplets ($\delta = 7.2$ Hz). As the temperature is raised the value for δ decreases, until at 85°C the resonances overlap, and only one 1:2:1 triplet is seen. The same behavior occurs for the compound $\text{Pd}(\text{PPhMe}_2)_2\{\text{C}(=\text{NC}_6\text{H}_{11})_2\text{CH}_3\}\text{I}$, with a coalescence at a higher temperature (130°C). Yamamoto and Yamazaki propose five-coordinate structures, (III), (IV), and (V), to rationalize this behavior. It must be observed, however, that any restriction of C—Pd rotation in these complexes, regardless of bonding of the nitrogen atom of the iminoacyl group to the metal or not, will in fact produce the same asymmetry, and should lead to the same observation. This point has been emphasized for several platinum-carbene complexes of dimethylphenylphosphine by Clark and Manzer (42). An X-ray crystallographic study would nonetheless be of value to confirm or deny the suggestion of five-coordination.

Crociani *et al.* (49) have described an interesting reaction between *cis*- $\text{Pt}(\text{PPh}_3)(\text{CNC}_6\text{H}_5)\text{Cl}_2$ and a variety of phenyl-metal complexes (HgPh_2 , PbPh_4 , PbPh_3Cl , SnPh_3Cl , BiPh_3). The product of these reactions is a dimeric complex $[\text{Pd}(\text{PPh}_3)\{\text{C}(=\text{NC}_6\text{H}_5)\text{C}_6\text{H}_5\}\text{Cl}]_2$, which certainly must arise via an intermediate phenylpalladium complex which rearranges with isocyanide insertion [Eq. (9)]. The latter complex reacts with further



phosphine, splitting the chlorine bridging units, to give $\text{Pd}(\text{PPh}_3)_2\{\text{C}(=\text{NC}_6\text{H}_5)\text{H}_5\}\text{Cl}$.

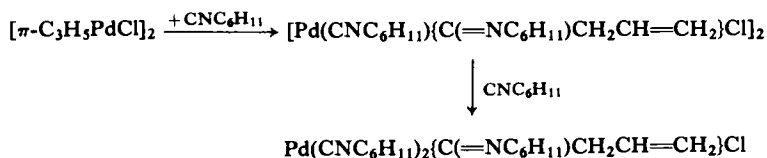
Additional work on alkyl platinum reactions has been completed which mostly supports the generality of these observed insertion reactions. Treichel and Wagner (153) have varied the choice of phosphine ligand; utilizing the complexes $\text{Pt}(\text{phos})_2(\text{CH}_3)\text{X}$ ($\text{phos} = \text{PEt}_3$, $\text{X} = \text{Br}$, I ; and $\text{phos} = \text{PPhMe}_2$, $\text{X} = \text{I}$) both ionic intermediate and inserted products were obtained.

Yamamoto and Yamazaki (171) carried out reactions of $\text{Pt}(\text{PEt}_3)_2\text{CH}_3\text{I}$ and $\text{Pt}(\text{PPhMe}_2)(\text{CH}_2\text{C}_6\text{H}_5)\text{I}$ with *tert*-butyl and cyclohexyl isocyanides. These reactions gave small yields of the ionic intermediate species, which readily reverted to the appropriate iminoacyl complexes. In reactions of analogous chloride complexes the intermediate species was not isolated. It is suggested on the basis of PMR data that these iminoacyl complexes are five-coordinate (see above).

A recent paper has now extended this work on insertions of isocyanides to $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$ ($\text{R} = \text{CH}_3, \text{CH}_2\text{C}_6\text{H}_5$) complexes (172). With $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_3$ and either CNBu^t or $\text{CNC}_6\text{H}_{11}$ one observes only the anticipated product, $\text{C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNR})\text{COCH}_3$. However, the benzyl-iron complex $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_2\text{C}_6\text{H}_5$ and CNBu^t gives a decarbonylated species $\text{C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNBu}^t)\text{CH}_2\text{C}_6\text{H}_5$, whereas with $\text{CNC}_6\text{H}_{11}$ the only product is $\text{C}_5\text{H}_5\text{Fe}(\text{CO})[(\text{C}=\text{NC}_6\text{H}_{11})_3\text{CH}_2\text{C}_6\text{H}_5]$; this latter compound has a structure analogous to (V).

It is appropriate to note that although the outlines of this type of chemistry seem straightforward, further examples are desired to establish some sort of generality in behavior. With further data it is possible that the minor differences in these reaction systems will begin to make sense. Furthermore, it should be pointed out that the reverse reaction, migration of an alkyl or aryl group from the acylimino group to a position of coordination to the metal, has not yet been observed. Decarbonylation, the analogous reaction in carbonyl systems, is well known.

In two instances (30, 74) insertion reactions involving allylpalladium complexes have been studied. Kajimoto *et al.* (74) first reported the reaction of $[\pi\text{-C}_3\text{H}_5\text{PdCl}]_2$ with cyclohexyl isocyanide (1:4 molar ratio) to give initially $[\text{Pd}(\text{CNC}_6\text{H}_{11})\{\text{C}(\text{C}=\text{NC}_6\text{H}_{11})\text{CH}_2\text{CH}=\text{CH}_2\}\text{Cl}]_2$; the chlorine bridging groups may cleave with the remaining ligand present [Eq. (10)].



(10)

Boschi and Crociani (30) were able to arrest this reaction (utilizing $\text{C}_6\text{H}_5\text{NC}$ and *p*- $\text{O}_2\text{NC}_6\text{H}_4\text{NC}$, however) at an earlier stage and isolate $\pi\text{-C}_3\text{H}_5\text{Pd}(\text{CNR})\text{Cl}$, from which $-\text{SnCl}_3$ and $-\text{GeCl}_3$ complexes were prepared by

standard means. From the phenyl isocyanide complex with additional isocyanide, a reaction analogous to that above was observed, giving $[\text{Pd}(\text{RNC})\{\text{C}(=\text{NC}_6\text{H}_5)\text{CH}_2\text{CH}=\text{CH}_2\}\text{Cl}]_2$, which was only stable enough to be characterized by infrared data. When $\pi\text{-C}_3\text{H}_5\text{Pd}(\text{CNC}_6\text{H}_4\text{NO}_2)\text{Cl}$ was treated with triphenylphosphine an analogous reaction occurred, giving $[\text{Pd}(\text{PPh}_3)\{\text{C}(=\text{NR})\text{CH}_2\text{CH}=\text{CH}_2\}\text{Cl}]_2$.

One other reaction deserves mention. From bis(cyclooctadiene)nickel and butadiene (31), and in the presence of an isocyanide (RNC, R = cyclohexyl, phenyl, *tert*-butyl) two organic oligomeric products are obtained, 1-acylimino-11-vinyl-3,7-cycloundecadiene and 1-acylimino-3,7,11-cyclododecatriene. In each, one isocyanide has been incorporated. An analogous reaction with carbon monoxide had been reported earlier. The proposed mechanism of these reactions, via a bis- π -allyl complex of nickel, is probably related to the mechanism described for allylpalladium complexes above.

One also observes that insertion reactions do not always occur, when perhaps they might be expected. For example, oxidative addition reactions of methyl iodide with $\text{Pt}(\text{CNBu}')_2(\text{PPh}_3)_2$ (85) and with several iridium d^8 complexes (50), and with $\text{Rh}(\text{PPh}_3)_2(\text{CNCH}_3)\text{Cl}$ (11) do not involve insertion reactions, although the products in the last of these reactions are still in some doubt. Addition reactions of $\text{Pt}(\text{L})_2\text{RX}$ ($\text{L} = \text{PEt}_3, \text{AsEt}_3$) with isocyanides in the presence of NaClO_4 lead to the isolation of $[\text{Pt}(\text{L})_2\text{-(CNR')R}]\text{ClO}_4$; and there is no report of isocyanide insertion into metal-alkyl bonds in these complexes (38, 39, 41).

B. Nucleophilic Reactions with Metal Isocyanide Complexes

The reactions of nucleophilic reagents with cationic and uncharged metal carbonyl complexes have received much attention in the past, and it is not surprising that these studies have now been extended to isocyanide metal complexes. Different products in these reactions can arise by three general routes; these include ligand substitution, reactions involving attack at a ligand, and reduction of the metal complex. All have been observed in reactions with metal isocyanide complexes.

The susceptibility of a metal complex to nucleophilic attack is enhanced by a positive charge on the complex. This fact, and the fact that most metal isocyanide complexes are cationic, probably explains why no nucleophilic reactions of uncharged isocyanide complexes have yet been reported. It is

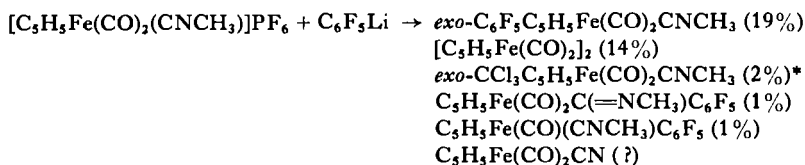
probable that such reactions will occur, however, at least using strong nucleophiles such as organolithium reagents. Analogous reactions with metal carbonyls are known.

There may be several limitations to the scope of this type of study with metal isocyanide species. Since generally the nucleophile bears a negative charge, reaction with a cationic species will decrease the positive charge on the metal. One has a suspicion, from the above arguments on bonding (Section II), that too radical a change in this direction may be undesirable. This could imply either that the reaction is not thermodynamically favorable, or that the reaction might instead occur with complex degradation. In support of this one notes that a number of stable metal isocyanides $[\text{Mn}(\text{CNCH}_3)_6]^+$, $[\text{Fe}(\text{CNCH}_3)_6]^{2+}$ seem quite reluctant to undergo simple reactions; forcing conditions eventually lead to decomposition (140). For comparison, one might choose $[\text{Mn}(\text{CO})_6]^+$ and $[\text{Mn}(\text{CNCH}_3)_6]^+$. The former is a quite reactive species toward halide $[\rightarrow \text{Mn}(\text{CO})_5\text{X}]$, hydroxide $[\rightarrow \text{Mn}(\text{CO})_5\text{H} + \text{CO}_2]$, and organolithium reagents $[\rightarrow \text{Mn}(\text{CO})_5\text{COR}]$, whereas the latter is apparently inert to these reactants (140).

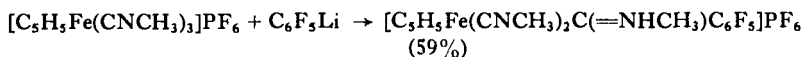
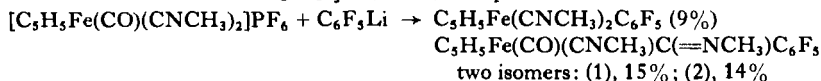
It may be noted that the additions of protonic molecules HA (alcohols, amines, thiols, etc.; see Section III,C) to isocyanides may be related to these reactions, in the formalistic sense anyway, since they involve additions of A^- (in conjunction with H^+) to the isocyanide. In a few instances the additions of HA can be accomplished by adding first A^- and then H^+ to the reactant species. However, no studies on HA additions have yet elucidated a mechanism for these reactions, so to draw a conclusion on the similarities of these reactions on mechanistic grounds is not appropriate. Because of this, and also for convenience, these subjects will be treated separately.

Several of the early nucleophilic reactions on a metal isocyanide complex were described by Pauson and Stubbs (112). The reaction of NaC_5H_5 and $[\text{Mn}(\text{CNC}_6\text{H}_5)_6]^+$ occurred with ligand displacement, and the product $\text{C}_5\text{H}_5\text{Mn}(\text{CNC}_6\text{H}_5)_3$ was isolated. Sodium borohydride and $\text{C}_5\text{H}_5\text{Fe}(\text{CO})-(\text{CNC}_6\text{H}_5)_3\text{I}$ give a complicated reaction, according to Joshi *et al.* (70); some reduction to dimeric $(\text{C}_5\text{H}_5\text{Fe})_2(\text{CO})_3\text{CNC}_6\text{H}_5$ is observed, however.

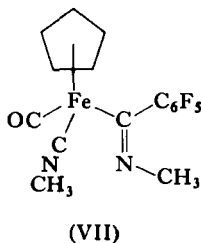
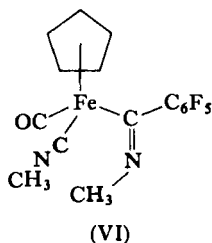
Reactions of the complexes $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_{3-x}(\text{CNCH}_3)_x]\text{PF}_6$ [$x = 1, 2$ (143), 3 (146)] with pentafluorophenyllithium have been carried out. For the mono- and diisocyanide complexes, several products were observed; the overall yield was generally low however. These reaction data are summarized by the equations below.



*CHCl₃ used in work-up.



Among the products in the reaction of $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{CNCH}_3)]\text{PF}_6$ the first, *exo*- $\text{C}_6\text{F}_5\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{CNCH}_3)$, is found in highest yield. It is interesting that analogous products are found in similar reactions with $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{phos}]\text{PF}_6$. The cyano complex, $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CN}$, apparently arises from dealkylation of the coordinated isocyanide ligand, a reaction which has subsequently been found to be more general (145). The reaction of $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNCH}_3)_2]\text{PF}_6$ occurs either with carbonyl displacement, or by reaction at an isocyanide ligand. The product of the latter reaction occurs as two isomers (VI, VII). The reaction of $\text{C}_6\text{F}_5\text{Li}$ and $[\text{C}_5\text{H}_5\text{Fe}(\text{CNCH}_3)_3]\text{PF}_6$ occurs exclusively at the ligand, but the resulting product is substantially basic (146), and abstracts a proton on work-up.

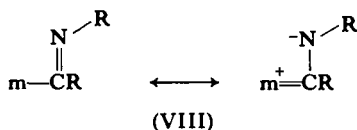


Reactions of $[\text{CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{NO})(\text{CO})(\text{CNCH}_3)]\text{PF}_6$ and $[\text{CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{NO})(\text{CNCH}_3)_2]\text{PF}_6$ occur in a similar fashion, and the products, $\text{CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{NO})(\text{CO})\{\text{C}(=\text{NCH}_3)\text{C}_6\text{F}_5\}$ in the former reaction and $\text{CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{NO})(\text{CNCH}_3)\{\text{C}(=\text{NCH}_3)\text{C}_6\text{F}_5\}$ in the latter, are isolated (20). The complex $\text{CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{NO})(\text{CNCH}_3)\{\text{C}(=\text{NCH}_3)\text{C}_6\text{F}_5\}$ picks up a proton, giving a mixture of this complex and the protonated species (146). The reactions of $[\text{C}_5\text{H}_5\text{W}(\text{CO})_3\text{CNCH}_3]\text{PF}_6$ and $[\text{C}_5\text{H}_5\text{W}(\text{CO})_2(\text{CNCH}_3)_2]\text{PF}_6$

with C_6F_5Li were also studied. In the former instance three products, $C_5H_5W(CO)_2(CNCH_3)COC_6F_5$, $C_5H_5W(CO)_2(CNCH_3)C_6F_5$, and $[C_5H_5W(CO)_3]_2$, were obtained. The latter reaction yielded only $C_5H_5W(CO)_2(CNCH_3)\{C(=NCH_3)C_6F_5\}$.

One must be somewhat reluctant to draw any far-reaching conclusions from the work to date. In general, there seems to be a predisposition for isocyanide ligand attack in these systems, although there are exceptions to this. Because of the low yields it is not possible to state with certainty a preferential position of attack for an entering nucleophile. In addition, the reactions described have been limited to C_6F_5Li as a nucleophile; it is possible that other organolithium compounds will react differently. For example, phenyllithium, in reactions with several cationic cyclopentadienyl-iron carbonyl complexes generally gives reduction to $[C_5H_5Fe(CO)_2]_2$, whereas for C_6F_5Li substitution is observed.

Perhaps one of the more striking observations in this work is the tendency for acylimino complexes to take up a proton (146), a feature not common to acyl complexes. The acylimino group nitrogen atom has a lone pair which possesses substantial basicity. The basicity is strongly a function of metal and ligand groups. Hence both $C_5H_5Fe(CNCH_3)_2\{C(=NCH_3)C_6F_5\}$ and $CH_3C_5H_4Mn(NO)(CNCH_3)\{C(=NCH_3)C_6F_5\}$ pick up a proton in work-up; however, $C_5H_5Fe(CO)(CNCH_3)\{C(=NCH_3)C_6H_5\}$ and $CH_3C_5H_4Mn(NO)(CO)\{C(=NCH_3)C_6F_5\}$ do not. Presumably the higher basicity of the former species is due to increased negative charge on the nitrogen arising from increased back-donation from the metal to the acylimino group (resonance form 2, VIII).

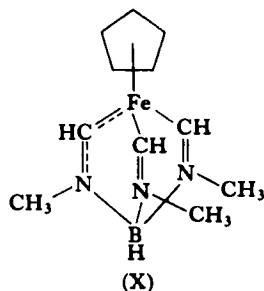
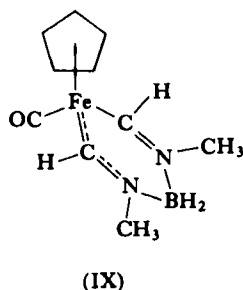


Protonation of the acylimino group in $Pt(PPh_3)_2\{C(=NCH_3)C_6H_5\}I$ by NH_4^+ and protonation of the bridging isocyanide in $(C_5H_5Fe)_2(CO)_3-(CNCH_3)$ by aqueous HCl were also noted (146). In addition, in several instances carbene complexes have been shown to undergo deprotonation-protonation reactions (46, 49, 100).

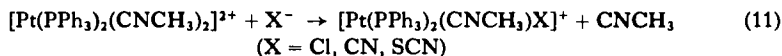
The reaction of $[C_5H_5Ni(PPh_3)CNC_6H_{11}]^+$ and phenyllithium gave two products, $C_5H_5Ni(PPh_3)C_6H_5$ and $C_5H_5Ni(CNC_6H_{11})\{C(=NC_6H_{11})-C_6H_5\}$ (164). Reactions with $[Pt(diphos)(CNCH_3)_2]^{2+}$ and C_6F_5Li or

CH_3Li gave only $\text{Pt}(\text{diphos})\text{R}_2$; with $[\text{Pt}(\text{PPh}_3)_2(\text{CNCH}_3)_2]^{2+}$ and $\text{C}_6\text{F}_5\text{Li}$ ligand displacement also occurred to give a mixture of $\text{Pt}(\text{PPh}_3)(\text{CNCH}_3)(\text{C}_6\text{F}_5)_2$ and $\text{Pt}(\text{PPh}_3)_2(\text{C}_6\text{F}_5)_2$ (147).

Borohydride additions to cationic isocyanide-metal complexes are also reported. Treichel, Stenson, and Benedict (148) describe the products $\text{C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CHNCH}_3)_2\text{BH}_2$, $\text{C}_5\text{H}_5\text{Fe}(\text{CHNCH}_3)_3\text{BH}$, $\text{CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{NO})(\text{CHNCH}_3)_2\text{BH}_2$, and $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2(\text{CHNCH}_3)_2\text{BH}_2$. Preliminary X-ray crystallographic data (54) confirm the suggested structures (IX) and (X). Attempted hydride abstraction from several of these complexes by $[\text{Ph}_3\text{C}]\text{BF}_4$ gave products where fluorine atoms had been exchanged for the hydrogens of the BH_2 groups. It is suggested that these reactions occur in two steps, hydride abstraction from the BH_2 group, followed by fluoride transfer to this boron from BF_4^- .

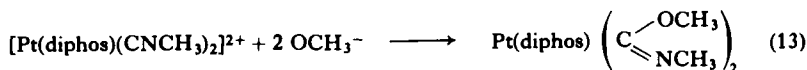
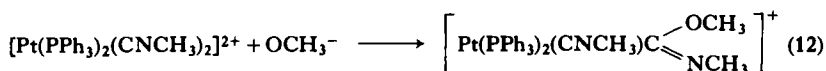


Reactions of a variety of weaker nucleophiles such as halide and pseudo-halide ions and $[\text{Pt}(\text{PPh}_3)_2(\text{CNCH}_3)_2]^{2+}$ have been studied (147) and, as might be expected, ligand replacement is usually observed [Eq. (11)].



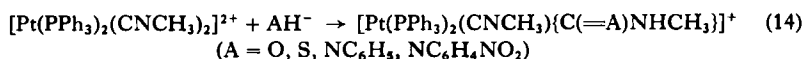
However, with bromide and iodide ions the five-coordinate adducts $[\text{Pt}(\text{PPh}_3)_2(\text{CNCH}_3)_2\text{X}]^+$ are isolated; the bromide complex loses isocyanide slowly but the iodide complex is stable. The analogous reactions with $[\text{Pt}(\text{diphos})(\text{CNCH}_3)_2]^{2+}$ give disubstitution.

In view of these results, the reactions of $[\text{Pt}(\text{PPh}_3)_2(\text{CNCH}_3)_2]^{2+}$ and $[\text{Pt}(\text{diphos})(\text{CNCH}_3)_2]^{2+}$ with alkoxide ion seem quite remarkable (147). Rather than displacing a ligand, the alkoxide ion adds to one or two coordinated isocyanide groups [Eqs. (12, 13)]. As one might suspect, the imino nitrogens in these products are basic, and can be protonated or alkylated.



The products from protonation are, of course, the same as those derived from additions of alcohols to the coordinated ligand (Section III,C).

The addition of hydroxide ion to $[\text{Pt}(\text{PPh}_3)_2(\text{CNCH}_3)_2]^{2+}$ is an anticipated extension of this work. The initial product of this reaction undergoes a tautomeric hydrogen shift, however, giving a platinum-carboxamido species (84, 149). Analogous additions of SH^- and NHR^- ($\text{R} = \text{C}_6\text{H}_5$, $\text{C}_6\text{H}_4\text{NO}_2$) are also observed [Eq. (14)]. The amidinium complexes ($\text{A} = \text{NR}$) can be



reversibly protonated at nitrogen (84, 149). However, protonation of the carboxamido complex leads to loss of methylamine and formation of a transient platinum(II) carbonyl species (not isolated) from which CO is displaced by the solvent. This reaction has some precedent in other work on carboxamido complexes.

It is interesting to observe that the addition reactions of OR^- and OH^- are not at all general for isocyanide complexes; indeed no additional examples of these reactions are known. A number of complexes, e.g., $\text{Mn}(\text{CNR})_6^+$ and $\text{Co}(\text{CNR})_5^+$ are reported to be inert to these reagents (90). In several other instances reduction of the metal complex by OH^- and OCH_3^- is observed. For example, in reactions of $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_{3-x}(\text{CNCH}_3)_x]^+$ ($x = 1, 2$), dimeric $(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_{4-y}(\text{CNCH}_3)_y$ ($y = 1, 2$) are observed (140). These reductions are anticipated as it is known that basic reagents can react with metal carbonyl complexes in the same manner [e.g., $\text{Fe}(\text{CO})_5 + \text{OH}^- \rightarrow \text{Fe}(\text{CO})_4\text{H}^- + \text{CO}_2$].

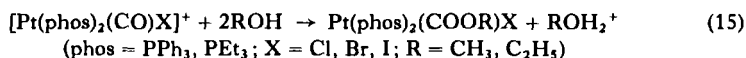
A number of studies have been reported concerning azide-isocyanide condensations to give tetrazoles. Early work by Beck and co-workers (18, 19) describes the addition of various isocyanides to metal azido species $[\text{Au}(\text{N}_3)_4]^-$, $[\text{Au}(\text{N}_3)_2]^-$, $\text{Au}(\text{PPh}_3)\text{N}_3$, and $\text{M}(\text{PPh}_3)_2(\text{N}_3)_2$, $\text{M} = \text{Pd}, \text{Pt}, \text{Hg}$. The products are carbon-bonded tetrazolato-metal complexes. It is not known whether metal isocyanide complexes are intermediates in these reactions. More recently inverse reactions with azide ion addition to metal isocyanide complexes were carried out, with similar results. From

$[\text{Pt}(\text{PPh}_3)_2(\text{CNCH}_3)_2]^{2+}$ and azide ion $[\text{Pt}(\text{PPh}_3)_2(\text{CNCH}_3)(\text{CN}_4\text{CH}_3)]^+$ is formed; and using $[\text{Pt}(\text{diphos})(\text{CNCH}_3)_2]^{2+}$ the product is $\text{Pt}(\text{diphos})-(\text{CN}_4\text{CH}_3)_2$ (147).

Azide ion additions to $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{CNCH}_3)]^+$ [giving $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2-\text{CN}_4\text{CH}_3$ and $\text{C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNCH}_3)\text{NCO}$], to $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNCH}_3)_2]^+$ [giving $\text{C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNCH}_3)\text{CN}_4\text{CH}_3$], to $[\text{CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{NO})\text{L}-(\text{CNCH}_3)]^+$, $\text{L} = \text{CO}$, PPh_3 [giving $\text{CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{NO})(\text{L})\text{CN}_4\text{CH}_3$], to $[\text{C}_5\text{H}_5\text{W}(\text{CO})_3(\text{CNCH}_3)]^+$ [giving $\text{C}_5\text{H}_5\text{W}(\text{CO})_2(\text{CNCH}_3)\text{NCO}$], and to $[\text{C}_5\text{H}_5\text{W}(\text{CO})_2(\text{CNCH}_3)_2]^+$ [giving $\text{C}_5\text{H}_5\text{W}(\text{CO})_2(\text{CNCH}_3)\text{CN}_4\text{CH}_3$] are reported (20).

C. Additions of Protonic Compounds to Coordinated Isocyanides

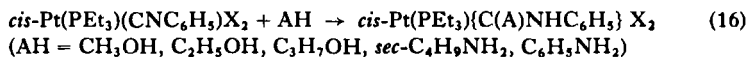
Perhaps the greatest excitement in the field of metal isocyanide complex chemistry has been generated by the observation that a variety of protonic substances (alcohols, thiols, amines, hydrazine) add to the coordinated isocyanide ligand. Interestingly, the reaction is one which has an analogy in carbonyl chemistry; Clark *et al.* (40) observed that the reactions of $[\text{Pt}(\text{phos})_2(\text{CO})\text{Cl}]^+$ and alcohols give $\text{Pt}(\text{phos})_2(\text{COOR})\text{Cl}$. Presumably this is an addition reaction, followed by deprotonation, the basicity of the carbonyl oxygen in the product being relatively low [Eq. (15)]. The scarcity



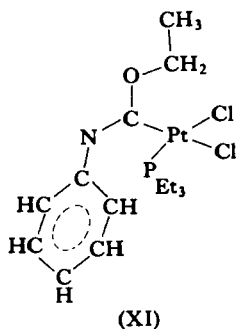
of analogous reactions involving carbonyls, however, has meant that this analogy has never been emphasized.

Although this work has so far been almost entirely devoted to platinum and palladium complexes, these addition reactions are now viewed as a general chemical phenomenon. However it may be appropriate to view this generality with caution, until further work appears.

The initial work in this field appeared as a communication in 1969 (8), and this work was later expanded to a full paper (9). Badley *et al.* described the synthesis of *cis*- $\text{Pt}(\text{PET}_3)(\text{CNC}_6\text{H}_5)\text{Cl}_2$ from $\text{Pt}_2(\text{PET}_3)_2\text{Cl}_4$ and the isocyanide; the bromide complex could be obtained from this complex by addition of bromide ion. These complexes were then observed to react with various substances [Eq. (16)]. A crystal structure study on the complex



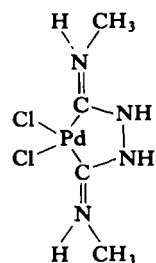
cis-Pt(PEt₃)[C(OEt)NHC₆H₅]Cl₂ was carried out, verifying its structure (XI).



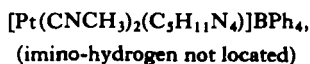
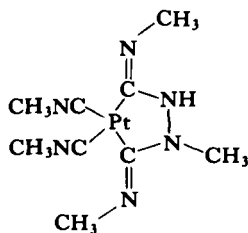
A structure study on *cis*-Pt(PEt₃)(CNC₆H₅)Cl₂ is also mentioned (10). In this compound a C—N—C angle of 165.5° is observed, rather a large deviation from the expected value of 180°. It is suggested that this geometry may in some way correlate with the reactivity with nucleophiles (OR⁻). However, data on structures for two other compounds, *cis*-Pt(PEt₃)(CNC₂H₅)Cl₂ and *cis*-Pt(CNC₆H₅)₂Cl₂, have now appeared (73). For these species more typical C—N—C angles near 175° are found. Since these compounds are also reactive toward nucleophiles, the correlation of bond angle and reactivity seems without merit.

Subsequent to the initial report by Badley *et al.* two communications appeared, which reported structural investigations on several products obtained from PtCl₄²⁻, methyl isocyanide, and hydrazine (33, 117); these compounds had previously been identified (incorrectly) as six-coordinate platinum(II) species (90). In addition, synthesis work in this area was extended somewhat further by these groups. The details of this work presented in these communications and in later full papers (34, 117) are summarized by Eqs. (17).

A structural study on the palladium complex PdCl₂(C₄H₁₀N₄) makes somewhat clearer the chemistry involved here (33, 34). The structure for this compound is shown in (XII), below; other complexes of the chelating ligand group C₄H₁₀N₄ are simply derived by substitution of L (or X⁻) for Cl⁻ in this structure, sometimes with concurrent loss of a proton. One or two hydrogen atoms [probably on ring nitrogens (117)] are protonic in character and may be lost in the presence of suitable strong bases. For example, for the diphos compound one can envision the following reversible proton addition



(XII)



(XIII)

Since the initial report on the addition reactions of palladium(II) and platinum(II) isocyanide complexes by Badley *et al.* (8), a rather substantial number of further examples have been reported. These are summarized in Table II.

In only two instances have additions to more than one isocyanide been observed (99, 147). There seems no reason not to expect this to occur, however, and, doubtlessly, more examples will be forthcoming.

The product $\text{Pt}(\text{PPh}_3)(\text{CNR})[\text{C}(=\text{NR})\text{OCH}_3]\text{Cl}$ ($\text{R} = p\text{-tolyl}$) was obtained from $\text{Pt}(\text{PPh}_3)_2\text{Cl}_2$, $p\text{-tolyl}$ isocyanide, and KOH in methanol (100). Its formation would seem to be related to the reactions described above; however, the base serves to deprotonate the resulting product. An analogous reaction of $\text{Au}(\text{PPh}_3)\text{Cl}$ to give $\text{Au}(\text{PPh}_3)\text{C}(=\text{NR})\text{OCH}_3$ was also described.

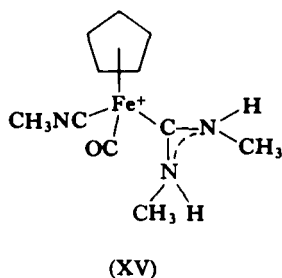
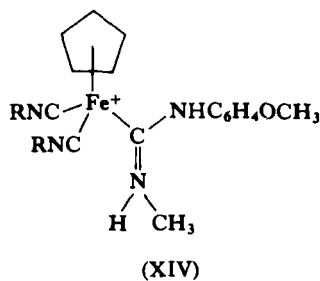
Angelici and Charley have shown that methyl and ethyl amines will add to one isocyanide in $[\text{C}_5\text{H}_5\text{Fe}(\text{CNC}_6\text{H}_4\text{OCH}_3)_3]^+$ (5) to give the product (XIV), which exists as two isomers. From $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNCH}_3)_2]^+$ and CH_3NH_2 the product is (XV) (3). Apparently only one isomer is formed, as the PMR spectrum shows three methyl resonances of equal intensity at τ 6.55, 6.92, and 7.27. It is interesting that the latter reaction occurs at an isocyanide, giving an amidinium complex, rather than at the CO group to give a carboxamido-iron compound.

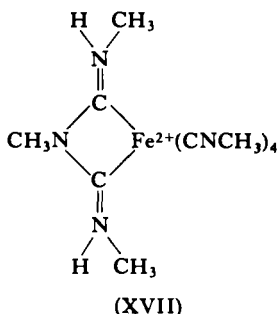
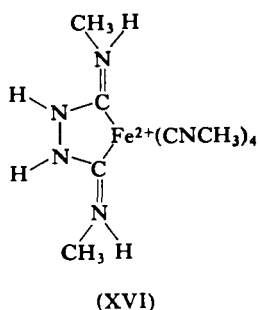
In addition, several addition reactions have been reported for the iron complex $[\text{Fe}(\text{CNCH}_3)_6]^{2+}$ with hydrazine and with methylamine (99); the products (XVI) and (XVII), respectively, are described. A crystal structure study on the latter compound was carried out.

TABLE II

ADDITIONS OF ALCOHOLS AND AMINES TO PLATINUM(II) AND PALLADIUM(II) COMPLEXES

Reactants	Products	References
<i>cis</i> -Pd(CNPh) ₂ Cl ₂ + CH ₃ OH	Pd(CNPh){C(=NPh)OCH ₃ }Cl ₂	48
+ tolNH ₂	Pd(CNPh){C(=NPh)NHtol}Cl ₂	25, 48
<i>cis</i> -Pd[PPh ₃](CNPh)Cl ₂ + CH ₃ OH	Pd(PPh ₃){C(=NPh)OCH ₃ }Cl ₂	48
+ tolNH ₂	Pd(PPh ₃){C(=NPh)NHtol}Cl ₂	25, 48
+ <i>p</i> -O ₂ NC ₆ H ₄ NH ₂ (RNH ₂)	Pd(PPh ₃){C(=NPh)NHR}Cl ₂	25
<i>cis</i> -Pt(CNCy) ₂ Cl ₂ + tolNH ₂	Pt(CNCy){C(=NHCy)NHtol}Cl ₂	25
+ CH ₃ OH	Pt(CNCy){C(=NHCy)OCH ₃ }Cl ₂	25, 27
+ C ₂ H ₅ OH	Pt(CNCy){C(=NHCy)OC ₂ H ₅ }Cl ₂	25
<i>cis</i> -Pt(CNtol) ₂ Cl ₂ + tolNH ₂	Pt(CNtol){C(=NHTol) ₂ }Cl ₂	25
+ CH ₃ OH	Pt(CNtol){C(=NHTol)OCH ₃ }Cl ₂	27
<i>cis</i> -Pt[PEt ₃](CNPh)Cl ₂ + ROH (CH ₃ OH, C ₂ H ₅ OH, C ₃ H ₇ OH)	Pt(PEt ₃){C(=NPh)OR}Cl ₂	8, 9
+ RNH ₂ (PhNH ₂ , <i>sec</i> -BuNH ₂)	Pt(PEt ₃){C(=NPh)NHR}Cl ₂	8, 9
<i>trans</i> -[Pt(PPh ₃) ₂ (CNCH ₃) ₂] ²⁺ + CH ₃ OH	[Pt(PPh ₃) ₂ (CNCH ₃){C(=NHCH ₃)OCH ₃ }] ²⁺	147
<i>cis</i> -[Pt(diphos)(CNCH ₃) ₂] ²⁺ + C ₂ H ₅ OH	[Pt(diphos){C(=NHCH ₃)OEt] ₂] ²⁺	147
<i>trans</i> -[Pt(PPhMe ₂) ₂ (CNEt) ₂] ²⁺ + C ₂ H ₅ OH	[Pt(PPhMe ₂) ₂ (CNEt){C(=NHEt)OC ₂ H ₅ }] ²⁺	42
+ RNH ₂ (C ₆ H ₅ NH ₂ , tolNH ₂)	[Pt(PPhMe ₂) ₂ (CNEt){C(=NHEt)NHR}] ²⁺	42
+ C ₆ H ₅ CH ₂ SH	[Pt(PPhMe ₂) ₂ (CNEt){C(=NHEt)SR}] ²⁺	42
[Pt(CNCH ₃) ₄] ²⁺ + CH ₃ NH ₂	[Pt{C(NHCH ₃) ₂ }] ²⁺	99





These studies, along with those of Angelici (3, 5) are the only significant excursions in this area of chemistry outside the palladium(II) and platinum(II) realm.

D. Copper-Catalyzed α -Additions to Isocyanide

Not a lot need be said on this subject, since a good recent review is available (156). However, there can be no doubt of the significance of this work, and its inclusion in a discussion of current and important topics is appropriate.

Various α -addition reactions are observed to be metal- or acid-catalyzed, or to be uncatalyzed. In this review only the metal-catalyzed reactions will be discussed, since it is generally assumed that metal isocyanide complexes are involved in these systems. A number of metal-catalyzed α -addition reactions have been mentioned recently. Copper(I) oxide seems to be the most commonly used catalyst, although other metal complexes sometimes are satisfactory. Table III presents a partial survey of this work.

As noted above, interest in metal-catalyzed reactions arises primarily from the assumption that metal isocyanide compounds are involved as reaction intermediates. Though this is an idea which intuitively has some merit, there is actually little in the way of experimental evidence to confirm or deny this. In favor of this postulate is the isolation of a metal isocyanide complex (in one instance only). This complex, having the formula $(\text{CuCl})_2(\text{CNC}_6\text{H}_{11})_2\text{HNC}_5\text{H}_{10}$ ($\text{HNC}_5\text{H}_{10}$, pip = piperidine) was obtained from a heterogeneous system involving CuCl , cyclohexyl isocyanide, and piperidine (124); it is unstable, decomposing slowly at room temperature to give $\text{C}_5\text{H}_{10}\text{NCH}=\text{NC}_6\text{H}_{11}$. No structure is proposed for the metal

The existence of copper(I) isocyanide complexes is well documented, of course (90). Such complexes are basically straightforward, having stoichiometries and physical and chemical properties analogous to other copper(I) complexes. It would be somewhat surprising if the studies currently underway on the catalytic systems had not attempted to sketch in this relationship more precisely. No copper(0) isocyanide complexes are known, so such species if they exist here would be particularly interesting; their stability is clearly low with respect to ligand dissociation, or they would have been isolated in these studies.

One might also draw attention to an analogous behavior apparently observed with silver. In two patents (176, 177) finely divided silver metal is observed to dissolve in liquid alkyl and aryl isocyanides to homogeneous solutions containing up to about 10% metal (by weight). These solutions conduct an electric current. On evaporation metallic silver is deposited.

In addition to α -additions to isocyanides, copper oxide-cyclohexyl isocyanide mixtures are catalysts for other reactions including olefin dimerization and oligomerization (121, 125, 126). They also catalyze pyrroline and oxazoline formation from isocyanides with a protonic α -hydrogen (e.g., PhCH_2NC or $\text{EtOCOCH}_2\text{NC}$) and olefins or ketones (130), and the formation of cyclopropanes from olefins and substituted chloromethanes (131). The same catalyst systems also catalyze Michael addition reactions (119a).

IV

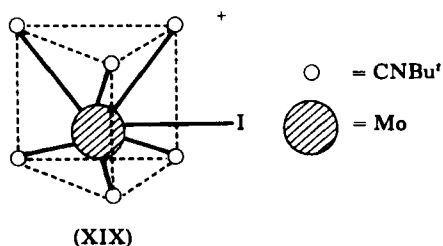
ISOCYANIDE COMPLEXES OF VARIOUS METALS

A. Group VIB

Isocyanide complexes of Group VIB metals which were described previously by Malatesta and Bonati (90) include: $\text{M}(\text{CNAr})_6$, $\text{M} = \text{Cr, Mo, W}$, prepared by reaction of a metal salt and an aryl isocyanide, with either a reducing agent present, or with a valence disproportionation of the metal occurring; $\text{M}(\text{CO})_{6-x}(\text{RNC})_x$, $\text{M} = \text{Cr, Mo, W}$, $x = 1, 2, 3$, from various ligand replacement reactions starting with the metal hexacarbonyl; $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_{3-x}(\text{RNC})_x\text{Y}$ ($\text{Y} = \text{halogen}$, $x = 1, 3$; $\text{R} = \text{C}_6\text{H}_5, \text{CH}_3$) from either displacement of carbonyl groups, or by alkylation of the appropriate cyano complex; $[\text{C}_5\text{H}_5\text{W}(\text{CO})_3\text{CNCH}_3]\text{I}$, from alkylation of $\text{C}_5\text{H}_5\text{W}(\text{CO})_3\text{CN}$; $\text{AreneCr}(\text{CO})_2\text{CNR}$ (several arenes) by ligand replacement; and

$\text{Mo}(\text{NO})_2\text{L}_2\text{Cl}_2$, from isocyanide ligand addition to $[\text{Mo}(\text{NO})_2\text{Cl}_2]_x$. These complexes are, in general, analogous to many known complexes of these metals with other ligands.

Some extension in synthetic chemistry of Group VIB complexes of isocyanides has evolved in the last five years. Of particular interest are several compounds, $[\text{Mo}(\text{CNBu}')_6\text{I}]\text{I}$ and $\text{Mo}(\text{CNR})_5\text{X}_2$ (R = cyclohexyl, X = Br, and R = *p*-tolyl, X = Cl and Br). The former complex, obtained as orange prisms, is reported to arise when solid $\text{Ag}_4\text{Mo}(\text{CN})_8$ is shaken with *tert*-butyl iodide for several days (86). A crystal structure determination by X-ray techniques reveals that this complex has the structure (XIX). The six isocyanide ligands are arranged in a distorted trigonal prismatic configuration around the metal and the iodide is centered over one square face. The latter complexes arise from reactions of $\text{Mo}(\text{CO})_4\text{X}_2$ species with the appropriate isocyanide (23). They are diamagnetic, and as formulated



correspond to the EAN rule. The chloro complex $\text{Mo}(\text{CNC}_6\text{H}_4\text{CH}_3)_5\text{Cl}_2$ is reported to dissolve in nitrobenzene to give a conducting solution, in which the solvated species $[\text{Mo}(\text{CNC}_6\text{H}_4\text{CH}_3)_5\text{Cl} \cdot \text{S}]^+$ (S = solvent) is suggested to be present; however, the bromo complexes are nonconducting.

Although these complexes arise from rather different reactions, one has the intuitive feeling that they are closely related, with differences in stoichiometry and structure dependent on the halide ion present. A similar situation is observed with platinum complexes, where reactions of bis(phosphine)platinum dichloride (PPh_3 , PEt_3) and dibromide with methyl isocyanide give four-coordinate species, $[\text{Pt}(\text{phos})_2(\text{CNCH}_3)_2\text{X}]\text{X}$ (X = Cl, Br), whereas the five-coordinate complexes $[\text{Pt}(\text{phos})_2(\text{CNCH}_3)_2\text{I}]\text{I}$ are isolated from reactions with the bis(phosphine)platinum diiodide (147). It is also appropriate to note that one may look at seven-coordinate molybdenum complexes as being made up of the hexakis(isocyanide) complex $\text{Mo}(\text{CNR})_6$ acting as a base, and a strong Lewis acid, I^+ ; this suggests that

a study of the interactions of $\text{Mo}(\text{CNR})_6$ with other strong acids should be attempted.

In connection with the above complexes, the work of Bamford *et al.* (12) might be noted. These workers observed that phenyl isocyanide complexes of chromium in chloroform will catalyze the radical polymerization of methyl methacrylate. They suggest a mechanism involving ligand dissociation followed by oxidation by CCl_4 of the metal complex to a divalent metal species (unspecified nature); this process gives $\text{CCl}_3\cdot$ radicals which initiate the polymerization. Presumably the metal complex could be $\text{Cr}(\text{CNPh})_5\text{Cl}_2$.

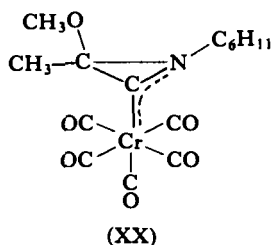
Several other new types of isocyanide complexes of these metals have been reported. McCleverty and James (97), studying the reaction of $[\text{C}_5\text{H}_5\text{Mo}(\text{NO})\text{I}_2]_2$ with various ligands, prepared the complex $\text{C}_5\text{H}_5\text{Mo}(\text{NO})(\text{CNC}_6\text{H}_4\text{OCH}_3)\text{I}_2$, and Green and Lindsell (62) observed that the protonation of $(\text{C}_5\text{H}_5)_2\text{W}(\text{OC}_2\text{H}_5)\text{CN}$ leads to $[(\text{C}_5\text{H}_5)_2\text{W}(\text{OC}_2\text{H}_5)(\text{CNH})]^+$ isolable as a hexafluorophosphate salt. Other workers have further extended known series of complexes. Benedict (20) prepared $[\text{C}_5\text{H}_5\text{W}(\text{CO})_2(\text{CNCH}_3)_2]\text{PF}_6$ and $[\text{C}_5\text{H}_5\text{W}(\text{CO})_2(\text{CNCH}_3)(\text{PPh}_3)]\text{PF}_6$ from $[\text{C}_5\text{H}_5\text{W}(\text{CO})_3\text{CNCH}_3]\text{PF}_6$ and methyl isocyanide and triphenylphosphine, respectively. He also observed that the reactions of $\text{C}_6\text{F}_5\text{Li}$ with $[\text{C}_5\text{H}_5\text{W}(\text{CO})_{4-x}(\text{CNCH}_3)_x]\text{PF}_6$ gave $\text{C}_5\text{H}_5\text{W}(\text{CO})_2(\text{CNCH}_3)\text{COC}_6\text{F}_5$ (for $x=1$) and $\text{C}_5\text{H}_5\text{W}(\text{CO})_2(\text{CNCH}_3)\text{C}(=\text{NCH}_3)\text{C}_6\text{F}_5$ (for $x=2$). With NaBH_4 and $[\text{C}_5\text{H}_5\text{W}(\text{CO})_3(\text{CNCH}_3)]\text{PF}_6$ a mixture of $[\text{C}_5\text{H}_5\text{W}(\text{CO})_3]_2$ and $(\text{C}_5\text{H}_5\text{W})_2(\text{CO})_5(\text{CNCH}_3)$ was formed. The reaction of NaBH_4 and $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2(\text{CNCH}_3)_2]\text{PF}_6$ gives $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2(\text{CHNCH}_3)_2\text{BH}_2$ (148).

The observation has been made (22) that $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2(\text{CNC}_6\text{H}_5)\text{I}$, formed from $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{I}$ and CNC_6H_5 , exists as two isomers. These can be separated; the *cis* isomer is pink, m.p. 78°C ; the *trans* is a peach color, m.p. 103°C . In solution at room temperature one isomer rapidly interconverts to the other, to give an equilibrium mixture with 60% *cis* and 40% *trans* species.

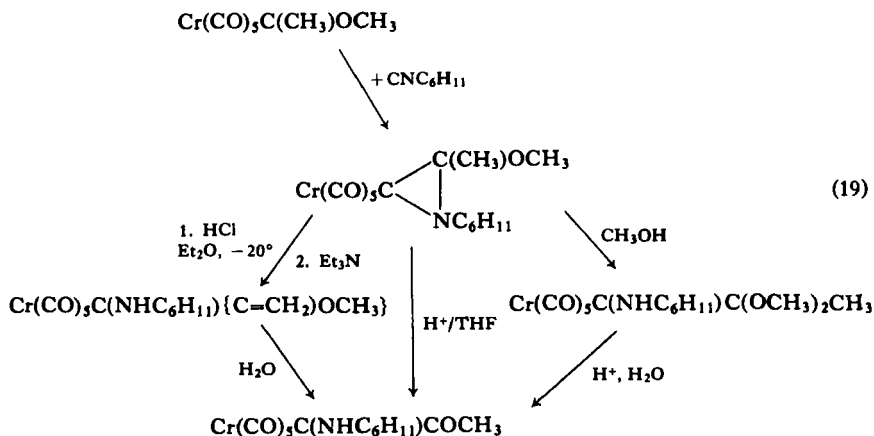
The syntheses of the complexes $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2(\text{CNR})\text{COR}'$ ($\text{R} = \text{Bu}^t$, cyclohexyl, 2,6-dimethylphenyl, $\text{R}' = \text{CH}_3$ and $\text{CH}_2\text{C}_6\text{H}_5$), $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{-C}(=\text{NCy})\text{CH}_2\text{Ar}$ (two isomers; $\text{Ar} = \text{C}_6\text{H}_5$, *p*- $\text{C}_6\text{H}_4\text{Cl}$, *p*- $\text{C}_6\text{H}_4\text{OCH}_3$); and $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2(\text{CNR})\text{CH}_2\text{C}_6\text{H}_5$ ($\text{R} = \text{Bu}^t$, 2,6-dimethylphenyl) (166, 167) were described earlier (Section III,A). Sato and co-workers (135) prepared several complexes of the formula triphenylene- $\text{Cr}(\text{CO})_2\text{L}$ ($\text{L} =$ various phosphines and CNC_6H_5), which are analogous to arene-

$\text{Cr}(\text{CO})_2\text{CNR}$ complexes described earlier by Strohmeier *et al.* (referred to in ref. 90). King and Efraty (82) report the synthesis of $(\text{C}_6\text{H}_5)_2\text{ECH}_2\text{CH}_2\text{NC}$ (L) (E = P, As) and their reactions with $\text{Cr}(\text{CO})_6$ to give $\text{L}_4\text{Cr}_3(\text{CO})_{12}$, having postulated structures involving three $\text{Cr}(\text{CO})_4$ units with terminal and bridging L groups.

Aumann and Fischer (7), as part of a larger project on carbene-metal complexes, have investigated the reaction of $\text{Cr}(\text{CO})_5\text{C}(\text{OCH}_3)\text{CH}_3$ and cyclohexyl isocyanide. They describe an initial 1:1 adduct of these reagents, to which they ascribe structure (XX); it is interesting to note that neither



carbonyl nor carbene are displaced in this reaction in contrast to reactions of some bases with this complex. This intermediate then can undergo a variety of reactions including the reactions with acids and base shown below [Eq. (19)]. Aumann and Fischer (7) also report, without experimental detail,



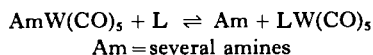
that pyrolysis of the carbene complex $\text{Cr}(\text{CO})_5\text{C}(\text{NHC}_6\text{H}_{11})\text{COCH}_3$ gives $\text{Cr}(\text{CO})_5\text{CNC}_6\text{H}_{11}$. This may be an interesting observation, in that it

appears to be the reverse of the well-documented addition reactions of various substances $R'H$ ($R' = RO-, RS-, RNH-,$ etc.) to isocyanides.

The reaction of hydroazoic acid and $[N(CH_3)_4][Cr(CO)_5\{COCH_2Si(CH_3)_3\}]$ might also be noted at this point (44). This reaction gives $Cr(CO)_5CNCH_3$ and $Cr(CO)_5NCCCH_3$, the former in larger quantity. It is suggested that this reaction involves a Schmidt-type rearrangement.

Kelly *et al.* (79, 80) observed that methyl isocyanide was reduced by nitrogen-fixing bacterial systems giving primarily methane, with a little ethylene and ethane. The subject of nitrogen fixation is being actively studied by a number of groups, of course, and several model systems which are active in the fixation of nitrogen have been reported (138, 157). The ability of these model systems to reduce isocyanides in the same manner as bacterial systems has been reported. Generally the model systems utilize a metal salt ($MoCl_5$, $Mo(acetylacetonate)_3$, $TiCl_3$, $FeCl_3$, etc.) and a strong reducing agent (Mg , sodium naphthalenide, $Na_2S_2O_4$). The molybdenum-containing systems are very effective for these reductions.

Several papers have appeared recently comparing various properties of carbonyl metal complexes substituted by various phosphines or phosphite ligands or isocyanides. Angelici and Ingemanson (4) studied the equilibrium



and found that the equilibrium constants for these systems decreased in the order $PBu_3 > P(OCH_2CH_2)_3CCH_3 > P(OBu)_3 > PPh_3 > \dots > P(OPh)_3 > p\text{-CNC}_6\text{H}_4\text{OCH}_3$. This is, of course, the same as the order of decreasing basicities of L , from which these authors conclude that the σ -bonding ability of the ligand appears to have the greatest influence over this trend. Guttenberger and Mueller (63) studied the infrared spectra of metal carbonyl complexes of various ligands including cyclohexyl isocyanide (and also C_6H_5CN , dimethyl sulfoxide, and ethylene sulfite). An order of π -donor strengths for the metal groups was ascertained by observing the changes in the value of ν_{CN} (or ν_{NC} and ν_{SO} for the other ligands). This trend in ν_{CN} for the isocyanide series is shown in Table IV.

Innorta, Distefano *et al.* (53, 72) have reported first ionization potentials for a series of $M(CO)_5L$ complexes (L = various phosphines and RNC) and find a linear correlation between these values and the ligand ionization potentials; and they report calculations of these ionization potentials using an equivalent orbital method.

TABLE IV
 ν_{CN} FOR SEVERAL CYCLOHEXYL ISOCYANIDE
 METAL COMPLEXES

Metal group, L_nM in $\text{L}_n\text{M}(\text{CNC}_6\text{H}_{11})$	ν_{CN} (cm^{-1})
$\text{Fe}(\text{CO})_4$	2186
$\text{Cr}(\text{CO})_5$	2168
$\text{Mo}(\text{CO})_5$	2167
(free $\text{CNC}_6\text{H}_{11}$)	(2158)
$\text{W}(\text{CO})_5$	2141
$\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2$	2120
$\text{C}_6\text{H}_5\text{Cr}(\text{CO})_2$	2083
$\text{C}_6\text{H}_3(\text{CH}_3)_3\text{Cr}(\text{CO})_2$	2044
$\text{C}_6(\text{CH}_3)_6\text{Cr}(\text{CO})_2$	2005

B. Group VIIB

Remarkably little work on isocyanide derivatives of the Group VIIB metals had appeared, apart from extensive studies on the $\text{M}(\text{CNR})_6^{n+}$ ($n = 1, 2$) complexes, when Malatesta and Bonati (90) reviewed this subject. Only one study of any depth had been reported. Joshi, Pauson, and Stubbs (70) observed that the reactions of phenyl isocyanide and the manganese pentacarbonyl halides give different products depending on the nature of the halide, and on the solvent used. They reported the following products: $[\text{Mn}(\text{CNC}_6\text{H}_5)_6]\text{Cl}$ from $\text{Mn}(\text{CO})_5\text{Cl}$ and $\text{C}_6\text{H}_5\text{NC}$ in tetrahydrofuran; $\text{Mn}(\text{CO})(\text{CNC}_6\text{H}_5)_4\text{I}$ from $\text{Mn}(\text{CO})_5\text{I}$ and this isocyanide in the same solvent; and four different products, $\text{Mn}(\text{CO})_3(\text{CNC}_6\text{H}_5)_2\text{Br}$ (refluxing ethanol), $\text{Mn}(\text{CO})_2(\text{CNC}_6\text{H}_5)_3\text{Br}$ (diglyme, 100°C), and a mixture of $\text{Mn}(\text{CO})(\text{CNC}_6\text{H}_5)_4\text{Br}$ and $\text{Mn}(\text{CNC}_6\text{H}_5)_5\text{Br}$ (refluxing tetrahydrofuran) from $\text{Mn}(\text{CO})_5\text{Br}$ and phenyl isocyanide.

Recently a further study of these reactions has been described (154). The compound originally characterized by Joshi *et al.* as $\text{Mn}(\text{CNC}_6\text{H}_5)_5\text{Br}$ was shown to be a mixture of $[\text{Mn}(\text{CNC}_6\text{H}_5)_6]\text{Br}$ and $[\text{MnCO}(\text{CNC}_6\text{H}_5)_3]\text{Br}$, by analyses and conductivity data. The white color reported for this complex is in accord with this new formulation; all of the other covalent complexes are yellow or gold. In view of the incorrect characterization of this complex, the isolation of the new complex $\text{Mn}(\text{CNC}_6\text{H}_5)_5\text{Cl}$ from

$\text{Mn}(\text{CO})_5\text{Cl}$ and CNC_6H_5 was particularly interesting. This compound was not reported by Joshi *et al.* (70).

TABLE V
THE REACTION OF MANGANESE CARBONYL HALIDES WITH CNC_6H_5 AND CNCH_3
(TETRAHYDROFURAN)^a

Reactants	Reaction conditions	Product
$\text{Mn}(\text{CO})_5\text{Cl} + \text{CNC}_6\text{H}_5(\text{L})$	Reflux, 4 hr	$\text{Mn}(\text{CO})\text{L}_4\text{Cl}$ (30%) MnL_5Cl (30%)
$\text{Mn}(\text{CO})_5\text{Br} + \text{CNC}_6\text{H}_5(\text{L})$	Reflux, 3 days	$[\text{MnL}_6]\text{Cl}$
	Reflux, 6 hr	$\text{Mn}(\text{CO})\text{L}_4\text{Br}$ (90%) $[\text{Mn}(\text{CO})\text{L}_5]\text{Br}$ (2%) $[\text{MnL}_6]\text{Br}$ (2%)
$\text{Mn}(\text{CO})_5\text{I} + \text{CNC}_6\text{H}_5(\text{L})$	Reflux, 3 hr	$\text{Mn}(\text{CO})_3\text{L}_2\text{I}$ (50%) $\text{Mn}(\text{CO})_3\text{L}_3\text{I}$ (15%)
	Reflux, 4 days	$\text{Mn}(\text{CO})\text{L}_4\text{I}$ (50%) $[\text{MnL}_6]\text{I}$ (25%)
$\text{Mn}(\text{CO})_5\text{Br} + \text{CNCH}_3(\text{L}')$	Room temp. 48 hr	$\text{Mn}(\text{CO})_3\text{L}'_2\text{Br}$ (63%)
	Reflux, 6 hr	$\text{Mn}(\text{CO})_2\text{L}'_3\text{Br}$ (85%)
	Reflux, 24 hr	$\text{Mn}(\text{CO})_2\text{L}'_3\text{Br}$ (40%) $\text{Mn}(\text{CO})\text{L}'_4\text{Br}$ (12%) $[\text{Mn}(\text{CO})\text{L}'_5]\text{Br}$ (18%)
$\text{Mn}_2(\text{CO})_8\text{Br}_2 + \text{CNCH}_3(\text{L}')$	Room temp. 3 hr	$\text{Mn}(\text{CO})_4\text{L}'\text{Br}$

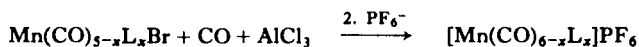
^a From ref. (154).

Information on product distributions (Table V) (154) for each reaction suggests that these reactions are not nearly so straightforward as suggested by Joshi *et al.* Obviously the time of the reaction is an important factor in determining the degree of substitution. Apart from the comments above, the discrepancies between the two references (69, 154) largely involves kinetics, and since neither group sought to carry out this study with sufficiently rigorous conditions to make a rate comparison possible, it is not appropriate to elaborate on the differences.

The reaction of $\text{Mn}(\text{CO})_5\text{Br}$ and methyl isocyanide was also carried out (Table V); the products are analogous to those obtained from phenyl isocyanide and the manganese complex.

A crystal structure study on *fac*- $\text{Mn}(\text{CO})_3(\text{CNCH}_3)_2\text{Br}$ has been done (133).

Mixed methyl isocyanide carbonyl manganese(I) cations $[\text{Mn}(\text{CO})_{6-x}\text{L}_x]\text{PF}_6$ ($\text{L} = \text{CNCH}_3$) were prepared by the standard method (154). The



cationic complexes of manganese can be oxidized electrochemically. The data given in Table I were obtained by Treichel and Dirreen (154).

Several comments on these data were presented earlier (Section II). One might make two further observations here. First, there is a general trend to higher $E_{1/2}$ values which is seen with progressive replacement of isocyanides by carbonyls. This means that these species are progressively less easy to oxidize. Second, a further oxidation for the complexes with 0, 1, and 2 carbonyls is observed. This oxidation was believed to be associated with the process $\text{MnL}_6^{2+} \rightarrow \text{MnL}_6^{3+}$.

The chemical oxidation of $[\text{MnL}_6]\text{Y}$ is well known. These voltammetric data suggested some of the other species might be successfully oxidized; indeed $[\text{Mn}(\text{CO})(\text{CNCH}_3)_5]\text{PF}_6$ was found to be oxidized to $[\text{Mn}(\text{CO})(\text{CNCH}_3)_5](\text{PF}_6)_2$ by nitric acid (154). The expected shift of ν_{CO} and ν_{CN} to higher frequencies in the dication is noted. Chemical oxidation to an MnL_6^{3+} species could not be accomplished, however.

It is also appropriate to observe the substantial difference in ease of oxidation between phenyl and methyl isocyanide complexes, which has obvious chemical implication. This may perhaps be rationalized on the basis that phenyl isocyanide is a better π -acceptor than methyl isocyanide. This conclusion had previously been reached by infrared studies (see Section II).

A number of other manganese isocyanide complexes have also been reported. Dimanganese decacarbonyl and methyl isocyanide (L) react in refluxing glyme to give $\text{Mn}_2(\text{CO})_7\text{L}_3$ and a second product, still uncharacterized (154). Trifluoroacetylmanganese pentacarbonyl and methyl isocyanide upon refluxing in tetrahydrofuran give a mixture of $\text{CF}_3\text{Mn}(\text{CO})_4\text{L}$ and $\text{CF}_3\text{COMn}(\text{CO})_3\text{L}_2$ (153). This reaction may be compared to the report (69) that reactions of phenyl- or methylmanganese pentacarbonyl and phenyl isocyanide fail to give alkyl or aryl manganese complexes, yielding instead, $\text{Mn}_2(\text{CO})_{10-x}(\text{CNC}_6\text{H}_5)_x$ ($x = 1, 2$).

Walker and Mawby (161) have studied reactions of π -arene- $\text{Mn}(\text{CO})_2\text{CN}$ (arene = mesitylene, C_6H_6) with HBF_4 to give π -arene- $\text{Mn}(\text{CO})_2\text{CNBF}_3$, and with $[(\text{C}_2\text{H}_5)_3\text{O}]\text{BF}_4$ and $[\text{Ph}_3\text{C}]\text{BF}_4$, to give the $[\pi$ -arene- $\text{Mn}(\text{CO})_2$ -

$\text{CNR}]^+$ species ($\text{R} = \text{C}_2\text{H}_5$ and $-\text{CPh}_3$). They also observe that BF_3 will coordinate with the nitrogen of cyano group to form π -arene- $\text{Mn}(\text{CO})_2\text{-CNBF}_3$; the ligand group $[\text{CNBF}_3]^-$ is isoelectronic to CNCF_3 . Treichel and Smith (152) have observed that one or two carbonyls in $[\text{C}_6\text{H}_6\text{Mn}(\text{CO})_3]\text{PF}_6$ are replaced by methyl isocyanide (L) to give $[\text{C}_6\text{H}_6\text{Mn}(\text{CO})_{3-x}\text{-L}_x]\text{PF}_6$. A hydrogen isocyanide derivative of $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$ has also been reported; this compound, $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{CNH}$, is formed on protonation of $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{CN}]^-$ (56). The mass spectrum of $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{-CNC}_6\text{H}_{11}$ is reported (101).

Mono-substituted derivatives of $[\text{C}_5\text{H}_5\text{Mn}(\text{NO})(\text{CO})_2]^+$ (32) and di-substituted (20, 146) derivatives of $[\text{CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{NO})(\text{CO})_2]^+$ have been prepared by direct reactions of the isocyanide and $[\text{C}_5\text{H}_5\text{Mn}(\text{NO})(\text{CO})_2]^+$ or $[\text{CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{NO})(\text{CO})_2]^+$. Brunner and Schindler (32) observe variations of ν_{CO} and ν_{NO} for the series $[\text{C}_5\text{H}_5\text{Mn}(\text{NO})(\text{CO})\text{L}]^+$ ($\text{L} =$ phosphines, and cyclohexyl isocyanide) in the order $\text{CNC}_6\text{H}_{11} > \text{P}(\text{OPh})_3 > \dots > (\text{PPh}_3)_3 > \text{P}(\text{Bu})_3$. Reactions of the mono- and disubstituted complexes with pentafluorophenyllithium (20, 146), and of the disubstituted species with borohydride (148) were noted above.

Matteson and Bailey (94) have prepared several vinyl isocyanide complexes, $\text{Mn}(\text{CNCH}=\text{CH}_2)_6^+$, $\text{Cr}(\text{CNCH}=\text{CH}_2)_6$, and $\text{Co}(\text{CNCH}=\text{CH}_2)_5^+$. They have also studied the electron exchange reactions (95) $\text{MnL}_6^+ \rightleftharpoons \text{MnL}_6^{2+} + e^-$ ($\text{L} = \text{EtNC}$, *tert*- BuNC , $\text{CH}_2=\text{CHNC}$, PhNC) by ^{55}Mn NMR, observing that the rate of exchange for the *tert*- BuNC complex is less than the rate for the less bulky EtNC ligand complex. They also note that $[\text{Mn}(\text{CNCH}=\text{CH}_2)_6]^{2+}$ is orange-red, and $[\text{Mn}(\text{CNPh})_6]^{2+}$ is an intense purple in contrast to the pale pink color of analogous alkyl isocyanide species. Both phenyl and vinyl isocyanide complexes are diamagnetic; dimeric structures are suggested to account for this fact.

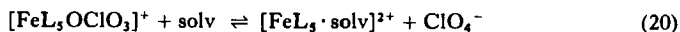
The only study on rhenium involves the alkylation of $\text{Ag}_4\text{Re}(\text{CN})_6$ and $\text{Ag}_3\text{Re}(\text{CN})_5\text{H}_2\text{O}$ with CH_3I in methanol, 85°C (134). The former reaction is said to give a compound, $\text{Re}(\text{CH}_3\text{NC})_4(\text{CN})_2$, which occurs in two forms, as a brown solid and as white crystals. Both forms are weakly paramagnetic, with magnetic moments of 0.45 and 0.47 BM. The latter reaction gives dark brown, solid $[\text{Re}(\text{CH}_3\text{NC})_5\text{H}_2\text{O}]\text{I} \cdot 4\text{AgI}$, which with nitric acid gives the complex $[\text{Re}(\text{CH}_3\text{NC})_5\text{H}_2\text{O}]\text{I}_2$, a red crystalline substance. Presumably these are isocyanide complexes rather than nitrile complexes as written in this reference.

Rhenium isocyanide complex chemistry has not been nearly so extensively studied as that of other elements and so further efforts are obviously necessary.

C. Iron, Ruthenium, and Osmium

Reactions of the ferrocyanide ion with alkylating agents, and reactions of iron(II) salts with alkyl or aryl isocyanides, have led to complexes of several types including $[\text{FeL}_6]^{2+}$, $[\text{FeL}_5\text{X}]^+$, *cis*- and *trans*- $\text{FeL}_4(\text{CN})_2$ and FeL_4X_2 ; this chemistry is reviewed by Malatesta and Bonati (90). There has been some extension of this work.

A reinvestigation of the presumed square-planar complexes $[\text{FeL}_4](\text{ClO}_4)_2$ has been carried out by Bonati and Minghetti (24). These complexes had previously been reported to be formed from anhydrous $\text{Fe}(\text{ClO}_4)_2$ and several aryl isocyanides (113). Repetition of the reaction of *p*-tolyl isocyanide and $\text{Fe}(\text{ClO}_4)_2$ failed to duplicate this observation, however. The products of this reaction depended on the conditions employed; and included $[\text{FeL}_6](\text{ClO}_4)_2$, from the reaction run without solvent; $[\text{FeL}_5\text{OCIO}_3]\text{ClO}_4 \cdot \text{H}_2\text{O}$, from the reaction in methylene chloride; $[\text{FeL}_5(\text{H}_2\text{O})](\text{ClO}_4)_2$ and $[\text{FeL}_6](\text{ClO}_4)_2$ when methanol was used as solvent. The formation of the hexakis(aryl isocyanide)iron(II) complex is of interest in that similar reactions of other iron salts with anions more capable of coordination to the metal give FeL_4X_2 . The σ -bonded perchlorate group in $[\text{FeL}_5\text{OCIO}_3]\text{ClO}_4$ is believed to be ionized in solvents such as CH_3CN or $\text{C}_6\text{H}_5\text{NO}_2$, according to conductivity and infrared data [Eq. (20)].

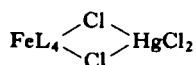


In another attempt to obtain a $[\text{FeL}_4]^{2+}$ species the reaction of FeL_4Cl_2 and NaClO_4 in acetone was attempted; this gave $[\text{FeL}_5\text{Cl}]\text{ClO}_4$, however (24).

Bonati *et al.* (26) have utilized the lability of the σ -bonded perchlorate in $[\text{FeL}_5\text{OCIO}_3]\text{ClO}_4 \cdot \text{H}_2\text{O}$ to prepare a series of complexes $[\text{FeL}_5\text{L}'](\text{ClO}_4)_2$ and $[\text{FeL}_5\text{X}]\text{ClO}_4$ [$\text{L} = \text{CNC}_6\text{H}_{11}$, CH_3CN , $\text{C}_6\text{H}_5\text{CN}$, Aph_3 ($\text{A} = \text{P}$, As , Sb); $\text{X} = \text{Cl}$, Br]; with 1,2-bis(diphenylphosphino)ethane (diphos) a μ -diphos complex is formed.

The adduct of FeL_4Cl_2 ($\text{L} = p\text{-tolylNC}$) and HgCl_2 (24, 89) was further studied; its structure in solution is suggested by Bonati and Minghetti (24) to be either $[\text{FeL}_4(\text{soln.})\text{Cl}]\text{HgCl}_3$, or $[\text{FeL}_4(\text{soln.})_x]\text{HgCl}_4$; there is a com-

plicated dependence of the conductivity on concentration. These authors prefer the solid state structure



over $\text{FeL}_4(\text{HgCl}_3)\text{Cl}$, although on intuitive grounds only; a preference for the latter structure is stated by Mays and Prater (96) (for the $\text{CNC}_6\text{H}_4\text{OCH}_3$ complex, however), also without experimental evidence.

The complex $\text{Fe}(\text{CNC}_6\text{H}_4\text{OCH}_3)_4\text{Cl}_2 \cdot \text{HgCl}_2$ in solution is quite reactive, with carbon monoxide or with additional isocyanide giving $[\text{FeL}_4(\text{CO})\text{Cl}]\text{-HgCl}_3$ or $[\text{FeL}_5\text{Cl}]\text{HgCl}_3$, respectively. However, the reaction with triphenylphosphine leads to precipitation of $[\text{PPh}_3\text{HgCl}_2]_2$ and formation of FeL_4Cl_2 , and reaction with SnCl_2 leads to $\text{FeL}_4(\text{SnCl}_3)_2$, via $\text{FeL}_4(\text{SnCl}_3)\text{Cl}$, and sequential reduction of HgCl_2 through Hg_2Cl_2 to elemental mercury (96).

The reaction of stannous chloride and *cis*- FeL_4Cl_2 ($\text{L} = \text{CNC}_6\text{H}_4\text{OCH}_3$) in chloroform gives two products, *cis*- $\text{FeL}_4(\text{SnCl}_3)\text{X}$ and *cis*- $\text{FeL}_4(\text{SnCl}_3)_2$. The latter may be converted to the *trans* isomer by refluxing in ethanol. If this reaction is run in acetone with added sodium perchlorate the complex $[\text{FeL}_5\text{SnCl}_3]\text{ClO}_4$ can be obtained (96).

The complexes $\text{Fe}(\text{CNR})_4(\text{CN})_2$ ($\text{R} = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5$) are reported to form 1:2 complexes with boron trihalides (65). In these complexes the BX_3 group coordinates to the cyanide nitrogen, giving the ligand group $[\text{CNBX}_3]^-$. A mention of a similar complex was made earlier (161).

A number of studies of the physical properties of the iron(II) isocyanide complexes have been reported. In particular, the Mossbauer spectra for these compounds have received much attention (13–17, 65, 91). The values for ν_{CN} for *cis*- and *trans*- $\text{Fe}(\text{CNCH}_3)_4(\text{CN})_2$ have been measured, and approximate force constants calculated for these complexes using the Cotton-Kraihanzel approximation (21). The values for ν_{CN} for *trans*- $\text{Fe}(\text{CNR})_4\text{Cl}_2$ ($\text{R} = \text{allyl}, \text{benzyl}, o\text{-tolyl}, p\text{-C}_6\text{H}_4\text{OCH}_3$) and for the ruthenium and osmium analogs were compared and these data translated into σ - and π -parameters for the ligand groups (78). The electronic spectra for the iso-electronic species $[\text{Fe}(\text{CNCH}_3)_6]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ and $[\text{Mn}(\text{CNCH}_3)_6]\text{I}$ were compared; from these data it was concluded that there is greater π -donation to the ligands in the manganese complex (55).

A crystal structure determination on *cis*- $\text{Fe}(\text{CNCH}_3)_4(\text{CN})_2 \cdot 4\text{CHCl}_3$ has been carried out (162).

Reactions of $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$, $\text{Ru}(\text{AsPh}_3)_2(\text{CH}_3\text{OH})\text{Cl}_2$, $\text{Ru}(\text{SbPh}_3)_3\text{Cl}_2$, or $\text{Ru}(\text{SbPh}_3)_4\text{Br}_2$ with ethyl isocyanide (115) give complexes of the formula $\text{Ru}[\text{A}(\text{C}_6\text{H}_5)_3]_2(\text{CNC}_2\text{H}_5)_2\text{X}_2$ ($\text{A} = \text{P, As, Sb}$). The single ν_{CN} in the infrared spectrum suggests a structure with *trans*-isocyanide groups. These complexes on heating to 240°C , or on refluxing in 2-methoxyethanol are converted to a second isomeric complex having two ν_{CN} absorptions; presumably in this isomer the isocyanides are in *cis* positions.

Not surprisingly, the addition of SnCl_2 to isocyanide-halo ruthenium complexes has been carried out (114); the complexes *cis*- $\text{Ru}(\text{CNC}_2\text{H}_5)_2(\text{APh}_3)_2\text{Cl}_2$ ($\text{A} = \text{P, As, Sb}$) add 1 mole of SnCl_2 , giving a complex believed to have the geometry shown in (XXI). There is a reference to $\text{Ru}(\text{CNC}_2\text{H}_5)_4(\text{SnCl}_3)_2$ in this article (114).

A paper describing this compound has just appeared (116). When yellow, *trans*- $\text{Ru}(\text{CNC}_2\text{H}_5)_4\text{Cl}_2$ is treated with SnCl_2 the compound *trans*- $\text{Ru}(\text{CNC}_2\text{H}_5)_4(\text{SnCl}_3)_2$ forms. A 1:1 adduct with mercuric chloride is also described. The structure of this complex in the solid state is not known. In nitromethane a conducting solution is obtained; it is suggested to contain the ions $[\text{Ru}(\text{CNC}_2\text{H}_5)_4(\text{solv})\text{Cl}]\text{HgCl}_3$.

Chatt, Melville, and Richards (36) carried out a number of reactions of $\text{Os}(\text{PR}_3)_3\text{Cl}_3$ and a reducing agent (Zn) in the presence of various ligands. Using methyl or phenyl isocyanides, two isomers having the formula $\text{Os}(\text{PPhMe}_2)_3(\text{CNR})\text{Cl}_2$ ($\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$) were formed; from the triethylphosphine compound, the $\text{Os}(\text{PEt}_3)_2(\text{CNCH}_3)_2\text{Cl}_2$ complex was obtained. Stereochemistries were assigned on the basis of the PMR spectra. The compound $\text{Os}(\text{PPhMe}_2)_3(\text{CNCH}_3)\text{Cl}_2$ was oxidized by chlorine to a paramagnetic monocation.

An additional report on an osmium isocyanide complex is found in conference abstracts (78).

Less has been done on the isocyanide derivatives of the iron carbonyls. However, several interesting references to isocyanide-substituted cyclopentadienyliron dicarbonyl dimers have appeared. The first report (70) was on $(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3\text{CNC}_6\text{H}_5$, which arises as a minor product from the borohydride reduction of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNC}_6\text{H}_5)\text{I}$. A crystal structure determination (71) by X-ray diffraction showed that the isocyanide ligand in this complex occupied a bridging position, confirming the structure predicted by infrared data. More recently Yamamoto and Hagihara (168) reported that the analogous cyclohexyl, *tert*-butyl, and benzyl isocyanide complexes may be formed by direct reaction of the isocyanide with

$[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$. The infrared spectrum of the benzyl isocyanide complex suggests that in the solid state the isocyanide is also in a bridging position but in benzene solution there is an equilibrium between this isomer and a second isomer with a terminal isocyanide ligand. The methyl isocyanide analog, also formed by the direct reaction of $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ and CNCH_3 (146) or by reduction of $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CNCH}_3]\text{PF}_6$ (140), appears to exist as the nonbridged isomer only. However, it readily rearranges on protonation to $[(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3\text{CNHCH}_3]^+$, which has a bridging >CNHCH_3 group.

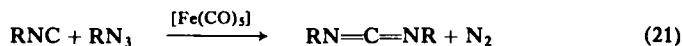
The crystal structure of an interesting complex, $\text{HFe}_3(\text{CO})_{10}\text{CN}(\text{CH}_3)_2$, has been reported (59). This species, which arises from the reaction of $\text{Fe}_3(\text{CO})_{12}$ and $\text{C}_6\text{H}_5\text{COCl}$ in dimethylformamide, has structure (XXII). This compound can be viewed as a derivative of the anion $\text{Fe}_3(\text{CO})_{10}^-(\mu\text{-CNCH}_3)\text{H}^-$, analogous to $\text{Fe}_3(\text{CO})_{11}\text{H}^-$. No doubt such an anion (as yet unknown) would be extremely basic, and readily alkylated.

The borohydride reactions (148) with $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_{3-x}(\text{CNCH}_3)_x]\text{PF}_6$ ($x = 2, 3$) have been noted above, as have the reactions of pentafluorophenyllithium with these species ($x = 1, 2, 3$) (143, 146).

Angelici and Charley (5) observed that methyl- and ethylamines add to one isocyanide ligand in $[\text{C}_5\text{H}_5\text{Fe}(\text{CNC}_6\text{H}_4\text{OCH}_3)_3]^+$, and methylamine adds to one isocyanide in $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNCH}_3)_2]^+$ (3), giving amidinium complexes. In addition, the reactions of hydrazine and methylamine with $[\text{Fe}(\text{CNCH}_3)_6]^{2+}$ have been carried out (99). This work is discussed in Section III, C.

The synthesis of $\text{Fe}(\text{CO})_4\text{CNC}_6\text{H}_{11}$ from $\text{Fe}(\text{CO})_5$ and cyclohexyl isocyanide upon ultraviolet irradiation has been reported (142) as has the synthesis of $\text{Fe}(\text{CO})_3(\text{CNtol})_2$ and $\text{Fe}(\text{CO})_4(\text{CNtol})$ from $\text{Fe}(\text{CO})_5$ and tol-N=PPh_3 (2a).

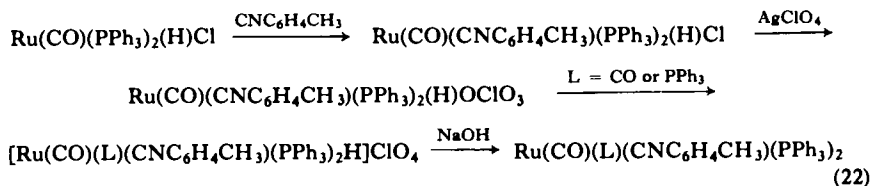
Iron pentacarbonyl has been shown to be a catalyst for the reaction of organic azides with isocyanides, giving carbodiimides (127) [Eq. (21)].



This reaction may involve an isocyanide metal complex as an intermediate species.

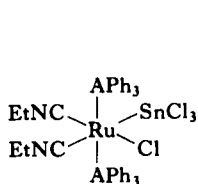
Until the appearance of a recent communication (37), no zero-valent ruthenium isocyanide complexes had been described. The synthesis of these complexes was accomplished by a lengthy reaction sequence, which was necessary since simple reactions such as substitution of a ligand in

$\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ with RNC , and reduction of $\text{Ru}(\text{CNR})_2(\text{PPh}_3)_2\text{Cl}_2$ were unsuccessful. The synthesis began with $\text{Ru}(\text{CO})(\text{PPh}_3)_3(\text{H})\text{Cl}$ in which an isocyanide was readily substituted for a phosphine; after successive treatment with AgClO_4 and a ligand (CO or PPh_3) one gets a cationic hydride complex which can be deprotonated [Eq. (22)]. In this fashion the zero-

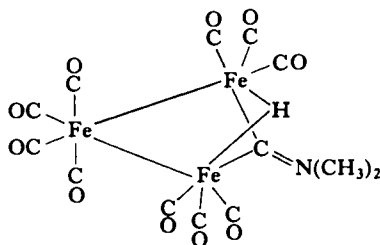


valent complexes $\text{Ru}(\text{CO})_2(\text{CNC}_6\text{H}_4\text{CH}_3)(\text{PPh}_3)_2$ and $\text{Ru}(\text{CO})(\text{CNC}_6\text{H}_4\text{CH}_3)(\text{PPh}_3)_3$ are obtained. The structures of these compounds are assumed to be (XXIII) and (XXIV).

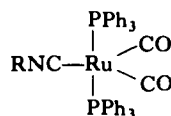
This proton transfer reaction is not fast, and it is suggested that this may be a more complicated reaction than was anticipated, perhaps occurring by initial addition of OH^- or OR^- to the metal followed by H_2O or ROH expulsion. In support of this is the isolation of a complex $\text{Os}(\text{CO})_2(\text{CNC}_6\text{H}_4\text{CH}_3)(\text{PPh}_3)_2(\text{H})\text{OR}$ from an analogous reaction sequence. (This is the only reference yet to any osmium carbonyl-isocyanide chemistry.)



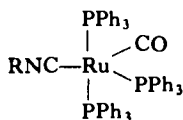
(XXI)



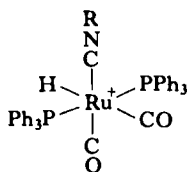
(XXII)



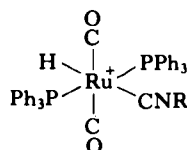
(XXIII)



(XXIV)



(XXV)



(XXVI)

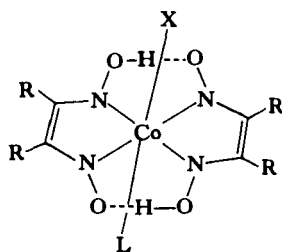
Reprotonation of $\text{Ru}(\text{CO})_2(\text{CNR})(\text{PPh}_3)_2$ gives $\text{Ru}(\text{CO})_2(\text{CNR})(\text{PPh}_3)_2\text{-H}^+$, which is an isomer of the previously described compound. The probable structures of the original isomer (XXV) and the second isomer (XXVI) are shown above.

D. Cobalt, Rhodium, and Iridium

A number of chemists have been interested in the chemistry of cobinamine and cobaloxime complexes of several ligands including isocyanides. Ablov *et al.* (1) have prepared a number of complexes $\text{CoX}(\text{DH})_2\text{L}$, where $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NO}_2$ and $\text{L} = \text{CNC}_6\text{H}_5$ and $\text{CNC}_6\text{H}_{11}$; and $\text{DH} =$ dimethylglyoximate; they also described analogous α -benzyldioximine complexes (2); see (XXVII). Herlinger and Brown (66) observed the formation of methylcobaloxime complexes $\text{CH}_3\text{Co}(\text{DH})_2\text{CNCH}_3$ and $\text{CH}_3\text{Co}(\text{DH})_2\text{CO}$; the methyl isocyanide complex is stable and does not undergo ligand exchange. The ν_{CN} frequency for the coordinated ligand in the methyl isocyanide complex is 2231 cm^{-1} vs. 2169 cm^{-1} for the free ligand, indicating that there is little π -bonding to the isocyanide in this complex. The values of ν_{CN} increased on coordination for the halo-cobaloxime species also, by about 100 cm^{-1} (1).

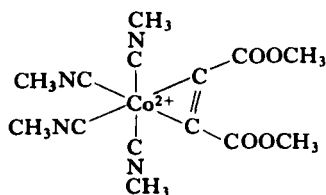
Schrauzer and Lee (136, 137) have studied the reaction of cyclohexyl isocyanide with the reduced form of vitamin B_{12} (B_{12r}); they find that this ligand will displace the 5,6-dimethylbenzimidazole group. Using the reduced form of cobaloxime (cobaloxime-II) as a model for the more complicated vitamin B_{12r} complex, they further extend this study. The presumably associated $[\text{Co}(\text{DH})_2]_x$ coordinates with one or two molecules of bases such as cyclohexyl isocyanide, the position of the equilibrium between the mono- and di-adducts being dependent on the free ligand concentration. The complex $[\text{Co}(\text{DH})_2\text{CNC}_6\text{H}_{11}]_x$, was isolated; it has a low magnetic moment (0.22 BM), suggesting association (dimerization) as a solid. In solution in DMF the molecular weight appears appropriate for a monomer but in 1,1-dichloroethylene this value is between that expected for monomer and dimer.

The $[\text{Co}(\text{DH})_2\text{L}]$ complexes react with oxygen (137) to give μ -peroxo complexes $\text{LCo}(\text{DH})_2\text{-O}_2\text{-Co}(\text{DH})_2\text{L}$, isolated using several ligands (not isocyanides however). These adducts are labile, and oxygen is easily lost. On standing these complexes can undergo oxidation, however, to μ -superoxo



(Cobaloximes, $R = CH_3$; α -benzyldioximines, $R = C_6H_5$)

(XXVII)



(XXVIII)

complexes which decompose to monomeric peroxo radical species $Co(DH)_2L(O_2)$. The ESR spectrum of one of the latter species ($L = CNC_6H_{11}$) is recorded.

The cobalt(II) isocyanide complexes $[Co(L)_5](ClO_4)_2$ are capable of coordinating to a sixth ligand (90). There is a recent report further documenting this behavior. From blue $[Co(CNC_6H_5)_5H_2O](ClO_4)_2$, water can be displaced by another phenyl isocyanide to give orange $[Co(CNC_6H_5)_6](ClO_4)_2$ which is stable only at $-50^\circ C$ or lower. The ESR spectrum of this complex was recorded (76).

The displacement of an isocyanide ligand in $[Co(CNCH_3)_5]^{2+}$ (blue, paramagnetic form) with acetylenes ($CH_3OCOC\equiv CCOOCH_3$, $CH_3C\equiv CCOOCH_3$, and $C_6H_5C\equiv CH$) has also been noted. The paramagnetic maroon solid, $[Co(CNCH_3)_4C_2(COOCH_3)_2][B(C_6H_5)_4]_2$, was isolated and assigned structure (XXVIII) (75).

Mixed phosphine isocyanide complexes $[Co(CNR)_3phos_2]^+$ and $[Co(CNR)_4diphos]^{3+}$, (the former were alluded to earlier (ref. 90, p. 185)), are reported to be obtained from $Co(phos)_2Cl_2$ and isocyanides (50). A vinyl isocyanide complex $[Co(CNC_2H_5)_5]^+$ is reported (94).

Several ESR studies of various cobalt(II) isocyanide complexes have been carried out (77, 81, 88). A Raman and infrared spectral study on $[Co(CNR)_5]-$

ClO_4 and on $[\text{Co}_2(\text{CNR})_{10}\text{I}](\text{ClO}_4)_3$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$) has been reported (28). The proposed structure for the latter complex, involving a linear Co—I—Co group, is supported by these data. The ultraviolet-visible spectra for $[\text{Co}(\text{CNCH}_3)_5]\text{ClO}_4$ has been studied (51). The crystal structure determination of *trans*- $\text{Co}(\text{CNC}_6\text{H}_4\text{CH}_3)_4\text{I}_2$ has been completed (58).

Yamamoto and Hagihara (165) observed that the reaction of $\text{Co}_2(\text{CO})_8$ and $\text{CNC}_6\text{H}_{11}$ in wet carbon tetrachloride gives CoL_4Cl_2 , CO , and $\text{Cl}_2\text{CHCONHC}_6\text{H}_{11}$; in methanol the organic product $\text{C}_6\text{H}_{11}\text{NC}=\text{C}(\text{OCH}_3)\text{CHCl}_2$ is obtained instead of the amide. They suggest that the reaction initially gives $[\text{CoL}_5][\text{Co}(\text{CO})_4]$, a valence disproportionation reaction observed with isocyanides (90) and with many other ligand groups; this complex then catalyzes the reaction of CCl_4 and $\text{CNC}_6\text{H}_{11}$ to give $\text{RN}=\text{C}=\text{CX}_2$, which adds H_2O (or methanol) to give the observed products.

The polymerization of allenes by $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ and a ligand (phosphines, arsines, amines, isocyanides) (175) and the polymerization of cyclohexyl isocyanide by $\text{Co}_2(\text{CO})_8$ (173) have been reported.

The most interesting work on the isocyanide complexes of the elements in this subgroup has been done with rhodium and iridium. For the most part, the work is involved with the oxidative addition reactions of d^8 square-planar metal complexes.

The preparations of a number of rhodium(I) complexes of isocyanides, some of them new, have been described. The new tetrakis(methyl isocyanide) complex, $[\text{Rh}(\text{CNCH}_3)_4]^+$, was isolated as salts of various anions from reactions of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ or $[(1,5\text{-C}_8\text{H}_{12})\text{RhCl}]_2$ and this isocyanide ligand (11), and several $[\text{Rh}(\text{CNR})_4]^+$ alkyl and aryl isocyanide complexes ($\text{R} = \text{Bu}^t, \text{Pr}^t, \text{C}_6\text{H}_{11}, p\text{-C}_6\text{H}_4\text{Cl}, p\text{-C}_6\text{H}_4\text{CH}_3$, and $p\text{-C}_6\text{H}_4\text{OCH}_3$) have been prepared starting with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (50). The iridium complex $[\text{Ir}(\text{CNBu}^t)_4]\text{Cl}$ was obtained from $\text{Ir}(\text{cyclooctene})_2(\text{CO})\text{Cl}$ (50) and *tert*-butyl isocyanide.

If $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and methyl isocyanide are reacted under mild conditions, and then I^- added, the rhodium(III) isocyanide complex $\text{Rh}(\text{CNCH}_3)_3\text{I}_3$ is obtained (11).

Several phosphine-isocyanide complexes of rhodium(I) and iridium(I) are also described. The complex $\text{Rh}(\text{PPh}_3)_2(\text{CNCH}_3)\text{Cl}$ is obtained from $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ and CNCH_3 (11). Addition of isocyanides to $\text{M}(\text{PPh}_3)_2(\text{CO})\text{Cl}$ ($\text{M} = \text{Rh}, \text{Ir}$) gave either $[\text{M}(\text{PPh}_3)_2(\text{CNR})_3]\text{Cl}$ ($\text{R} = p\text{-C}_6\text{H}_4\text{CH}_3$) or $[\text{M}(\text{PPh}_3)_2(\text{CNR})_2]\text{Cl}$ ($\text{R} = \text{Bu}^t$) or a mixture of both ($\text{R} = \text{Pr}^t, p\text{-C}_6\text{H}_4\text{Cl}$); the four-coordinate complex was slowly converted to the five-coordinate

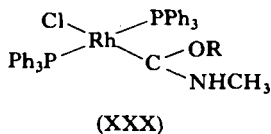
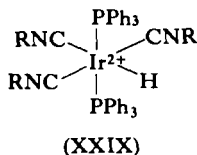
species on prolonged contact with excess isocyanide (50). Four-coordinate complexes of the latter type had been known before (90).

Oxidative additions to $[M(CNR)_4]Y$, $[M(CNR)_{2,3}(PPh_3)_2]Y$, and to $Rh(PPh_3)_2(CNCH_3)Cl$ have been carried out. The complex $Rh(PPh_3)_2(CNCH_3)Cl$, reported to be more reactive than the analogous carbonyl complex, adds iodine, $HgCl_2$, tetracyanoethylene, and oxygen. The oxygen addition is reversible and the complex was not isolated (11). However, it appears that analogous oxygen complexes, $RhL_2(CNR)X \cdot O_2$ ($X = Cl, Br, I$; $L = PPh_3, AsPh_3$; $R = C_6H_{11}, p-C_6H_4CH_3, Bu^t$), are isolable (102). The complexes $[M(CNCH_3)_4]BPh_4$ also undergo addition reactions to give $[Rh(CNCH_3)_4XY]BPh_4$; adducts of iodine and methyl iodide have been isolated (11). Analogous reactions (50) with complexes $[Rh(CNR)_4]PF_6$ (using several other isocyanides) have been carried out with C_3F_7I , CH_3I , I_2 , Br_2 , CH_3COCl , allyl chloride, $HgCl_2$, $SnCl_4$, $Sn(C_6H_5)_3Cl$, and $BrCN$. With $NOPF_6$ the cation $[Rh(CNR)_4NO]^{2+}$ is formed. The chloride salts $[Rh(CNR)_4]Cl$ reacted differently with X_2 , giving $[Rh(CNR)_2X_2Cl]_2$, presumed to be analogous to $[Rh(CO)_2Cl_3]_2$.

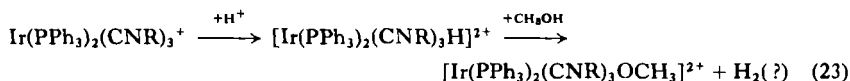
The mixed phosphine isocyanide complexes also undergo oxidative addition reactions, but the reactions were somewhat less predictable (50). The four-coordinate species $[Rh(PPh_3)_2(CNR)_2]^+$ gives a methyl iodide adduct $[Rh(PPh_3)_2(CNR)_2(CH_3)I]^+$. However, the five-coordinate species $[Ir(PPh_3)_2(CNR)_3]^+$ reacted with halogens, with phosphine elimination, to form sequentially $[Ir(PPh_3)_2(CNR)_3X]^{2+}$, $[Ir(PPh_3)(CNR)_3X_2]^+$, and $[Ir\{(CNR)_3X_2\}_2]^{2+}$. The analogous *tert*-butyl and isopropyl isocyanide complexes with methyl iodide gave $[Ir(PPh_3)(CNBu^t)_3(CH_3)I]^+$ and $[Ir(PPh_3)_2(CNPr^t)_2(CH_3)I]^+$, respectively (50). With allyl chloride the *t*-butyl isocyanide complex gave a mixture of the two types of complexes.

Additions of tetracyanoethylene (TCNE) to $[Rh(PPh_3)_2(CNC_6H_5)_2]Cl$ and to $[Rh(CNC_6H_5)_4]Cl$ gave $Rh(PPh_3)(CNC_6H_5)_2(TCNE)Cl$, and $Rh(CNC_6H_5)_3(TCNE)Cl$. The complex $Rh(CO)(p-CNC_6H_4OCH_3)_2Cl$ reacts with TCNE with carbonyl expulsion to give $Rh(TCNE)(p-CNC_6H_4OCH_3)_2Cl$, which can then add 1 mole of pyridine (29).

The five-coordinate iridium complexes may be protonated by glacial acetic acid, yielding $[Ir(PPh_3)_2(CNR)_3H]^{2+}$; the structure of this complex is determined by PMR measurements to be (XXIX). However, in the analogous HCl reaction $[Ir(PPh_3)_2(CNR)_2Cl_2]^+$ is obtained. The reaction of $[Ir(PPh_3)_2(CNR)_3]^+$ with methanol also proved quite out of the ordinary,

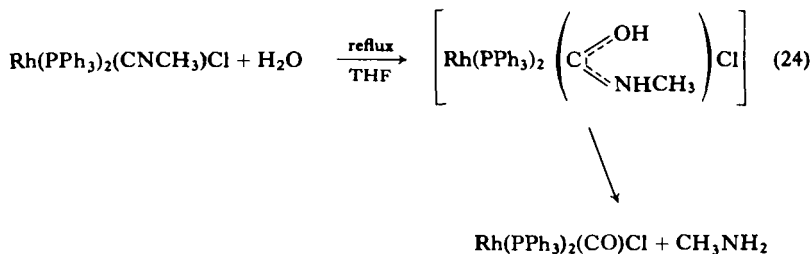


giving $[\text{Ir}(\text{PPh}_3)_2(\text{CNR})_3(\text{OCH}_3)]^{2+}$. It is suggested that this reaction (and also the HCl reaction) occurs with initial protonation, followed by nucleophilic attack with OCH_3^- (or Cl^-), and elimination of H^+ and phosphine or isocyanide (50). This would not account for the oxidation occurring, however (i.e., elimination of H^+ from $[\text{Ir}(\text{PPh}_3)_2(\text{CNR})_3(\text{H})(\text{OCH}_3)]^+$ would give $[\text{Ir}(\text{PPh}_3)_2(\text{CNR})_3\text{OCH}_3]^0$, not $[\text{Ir}(\text{PPh}_3)_2(\text{CNR})_3(\text{OCH}_3)]^{2+}$). An alternative [Eq. (23)] might be



There may be a similarity in these reactions with iridium and those reported with ruthenium and osmium (37). In the reactions of $[\text{Ru}(\text{PPh}_3)_3(\text{CNR})(\text{CO})\text{H}]^+$ or $[\text{Ru}(\text{PPh}_3)_2(\text{CNR})(\text{CO})_2\text{H}]^+$ with OH^- or OR^- the nucleophile is suggested to replace a ligand to give an initial product which then eliminates H_2O or ROH . The important fact here is that the attack of OR^- or OH^- at the metal has some precedent for these second and third transition series metals, whereas such reactions are improbable for metals of the first transition series. This reaction is also not analogous to that observed with the related carbonyl complex, for which ligand attack by OCH_3^- occurs, giving $\text{Ir}(\text{PPh}_3)_2(\text{CO})_2\text{COOCH}_3$.

One should also note the hydrolysis of $\text{Rh}(\text{PPh}_3)_2(\text{CNCH}_3)\text{Cl}$, which gives $\text{Rh}(\text{PPh}_3)_2(\text{CO})\text{Cl}$ (11). This reaction is suggested to occur by addition of H_2O to the coordinated isocyanide followed by elimination of methylamine [Eq. (24)].



As the reaction of metal-carboxamido complexes (e.g., $[\text{Pt}(\text{PPh}_3)_2(\text{CNCH}_3)(\text{CONHCH}_3)]^+$) with proton donors proceed in the same way $\rightarrow [\text{Pt}(\text{PPh}_3)_2(\text{CNCH}_3)(\text{CO})]^{2+}$ (147) the product of this reaction is not unexpected. One notes that relatively severe conditions are employed in this reaction (11).

Alcohol adds to the coordinated isocyanide in $\text{Rh}(\text{PPh}_3)_2(\text{CNCH}_3)\text{Cl}$ to give the complex (XXX) (11).

The reactions of the iridium hydride complexes IrL_2H_3 ($\text{L} = \text{PEt}_3$, PPhEt_2) with various ligands including isocyanides (L') give primarily *mer*- $\text{IrL}_2(\text{L}')\text{H}_3$, along with a small amount of the *fac* isomer (92, 93). However, the same reaction with $\text{L} = \text{AsPh}_3$ is said to give the *fac* isomer only (6).

E. Nickel, Palladium, and Platinum

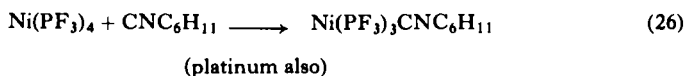
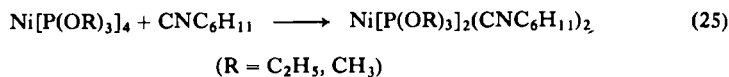
The most extensive study of isocyanide complexes of any group of metals has been accorded to these three metals, and a particularly elaborate chemistry has thus evolved. The extent of this work is all the more striking because very little work of outstanding interest had appeared up to about five years ago. At that time numerous complexes were known (90), almost all of which fit into quite typical stoichiometries: NiL_4 and $\text{NiL}_{4-n}\text{L}'_n$; ML_2X_2 and $[\text{ML}_4][\text{MX}_4]$ ($\text{M} = \text{Pt}, \text{Pd}$; $\text{L} = \text{an isocyanide}$; $\text{L}' = \text{another ligand group}$; $\text{X} = \text{halogen, pseudohalogen, etc.}$). It is reasonable to assume that these complexes, similar to many complexes with other ligand groups, would attract little attention.

The only work apparently contrary to this generalization involved the complexes $[\text{Pd}(\text{CNR})_2]_x$, whose stoichiometry was unusual and whose structure was unknown (and still is), and the platinum(II) hydrazine complexes, mentioned earlier (90).

Virtually all work on nickel isocyanide complexes centers on nickel(0) species. Malatesta and Bonati (90) describe complexes of the formula NiL_4 and $\text{Ni}(\text{CO})_x\text{L}_{4-x}$. The former are formed in a variety of reactions, including reductions of nickel(II) in the presence of isocyanides, and by the replacement of other ligands by isocyanides. The latter are, of course, derivatives of $\text{Ni}(\text{CO})_4$. In addition, a few ill-defined nickel(II) complexes are reported, as is the formally nickel(I) species $(\text{C}_5\text{H}_5\text{NiCNC}_6\text{H}_5)_2$.

Several studies have expanded this work on nickel(0) complexes somewhat. Substituted $\text{NiL}_3\text{L}'$ complexes ($\text{L} = \text{CNBu}$, CNPr^t , $\text{CNC}_6\text{H}_{11}$;

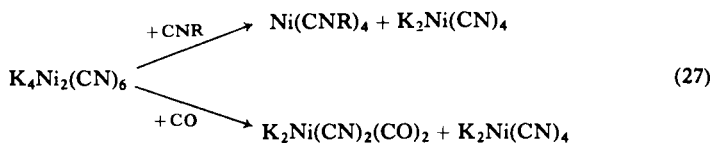
$L' = \text{PPh}_3, \text{AsPh}_3$) were reported from direct reaction of the phosphine or arsine and NiL_4 (104). Phosphite (98) and PF_3 (68) derivatives were also reported, formed from the tetrakis(phosphite) or tetrakis(PF_3)-nickel(0) species and an isocyanide [Eqs. (25, 26)].



For each of these reactions kinetic data were obtained. The reactions were first order in complex concentration, and zero order in isocyanide, as expected. The complex $\text{Ni}(\text{CNBu}')_4$, and presumably other $\text{Ni}(\text{CNR})_4$ complexes as well, undergo ligand dissociation in solution. In benzene solution, a molecular weight determination for this compound gives a low value (110). This is in accord with the presumed mechanism of substitution.

Several other complexes, $\text{M}(\text{CNBu}')_3\text{L}$ ($\text{L} =$ an activated olefin), have also been reported recently (110). This group of complexes, with the ligands (L) including maleic anhydride, fumaronitrile, and tetracyanoethylene, arises from isocyanide ligand substitution by the olefin. Less active olefins such as ethylene and diphenylacetylene, and azobenzene did not react.

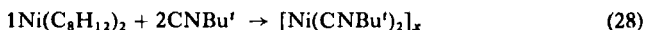
Nast *et al.* (105) studied the reaction of $\text{K}_4\text{Ni}_2(\text{CN})_6$ and various isocyanides (L) and found this to be an ideal means of obtaining the NiL_4 species. At the same time the reaction of this nickel cyanide complex with CO was also reinvestigated. There is a literature report that this reaction gives $\text{K}_4\text{Ni}_2(\text{CN})_6(\text{CO})_2$, but the latter species was incorrectly identified, and was found by Nast and co-workers to be a 1:1 mixture of $\text{K}_2\text{Ni}(\text{CN})_4$ and $\text{K}_2\text{Ni}(\text{CN})_2(\text{CO})_2$ [Eq. (27)].



A few comments on infrared spectra of these substituted nickel(0) isocyanides should be mentioned. Haas and Sheline (64) measured ν_{CO} for

the series of compounds $\text{Ni}(\text{CO})_{4-x}(\text{CNCH}_3)_x$ $x = 1 \rightarrow 4$; these data correspond well to earlier data of a similar nature (90). The ν_{CN} frequency in $\text{Ni}(\text{PF}_3)_3\text{CNC}_6\text{H}_{11}$ (68) is found at 2169 cm^{-1} , vs. 2138 cm^{-1} for the free ligand; from this, it was concluded that there is little π -donation from nickel to the isocyanide ligand. In accord with this conclusion the values for $\nu_{\text{P-F}}$ in this compound are found at a lower frequency.

Some of the most interesting work on nickel(0) complexes has been carried out by Otsuka *et al.* (107, 110). These workers have succeeded in obtaining a complex, $[\text{Ni}(\text{CNBu}')_2]_x$. This complex is prepared from bis(1,5-cyclooctadiene)nickel and the isocyanide, carefully restricting the amount of the latter to 2 moles per mole of nickel [Eq. (28)].



Obviously if a larger amount of isocyanide is used the more common stoichiometry, NiL_4 , results.

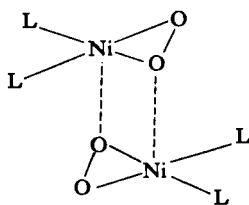
Otsuka *et al.* (107) describe $[\text{Ni}(\text{CNBu}')_2]_x$ as a reddish brown microcrystalline substance, which is extremely air-sensitive. It can be recrystallized from ether at -78°C , and is soluble in benzene; in the latter solution the infrared spectrum (2020s, br, 1603m, 1210m) and proton NMR (three peaks of equal intensity at τ 8.17, 8.81, and 8.94) were obtained. Neither analytical data nor molecular weight is available on this complex. The metal-ligand stoichiometry is presumably established by virtue of the molar ratio of reactants and by the stoichiometries of various reaction products.

It is suggested that the compound has some sort of cluster structure, and that both terminal and bridging isocyanide ligands are present. Thus the infrared peaks at 2020 and 1603 cm^{-1} can be assigned to these two types of groups; the complex NMR pattern would not be unexpected. It would be an attractive assumption that this complex is analogous in structure to the palladium complexes, $[\text{Pd}(\text{CNR})_2]_x$, which have been known for some time. Indeed the infrared spectrum of $[\text{Pd}(\text{CNBu}')_2]_x$ is somewhat similar, having absorptions at 2108 and 1700 cm^{-1} ; the differences in positions of these bands for the nickel and palladium complexes are a little larger than expected, however.

One ought to observe that only this single example using *tert*-butyl isocyanide, $[\text{Ni}(\text{CNBu}')_2]_x$, is known, as yet. It would obviously be desirable to prepare further examples of complexes of this type, and to attempt to establish a structure, presumably by X-ray crystallography.

The complex $[\text{Ni}(\text{CNBu}')_2]_x$ is reactive, as expected, and may be used as a

precursor for a number of new complexes. The reaction with oxygen is particularly interesting. If the reaction is run in ether at -20°C or lower, one can isolate an oxygen adduct, $(\text{tert-BuNC})_2\text{NiO}_2$ (107), presumably analogous to the known $(\text{PPh}_3)_2\text{NiO}_2$. The same reaction occurs with $[\text{Pd}(\text{CNR})_2]_x$. The nickel isocyanide-oxygen compound is stable as a solid to about 60°C , and appears to be associated in this state; a structure involving intermolecular axial interaction between metal and oxygen is suggested (XXXI). In solution the association is not maintained; presumably solvated



(XXXI)

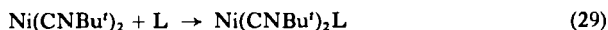
complexes, $\text{Ni}(\text{CNR})_2\text{O}_2(\text{solv})$ or $\text{Ni}(\text{CNR})_2\text{O}_2(\text{solv})_2$, are formed. In conjunction with this, compounds of both these types arise in reactions of $\text{Ni}(\text{CNBu}')_2\text{O}_2$ with CH_3NC . With methyl isocyanide at -19°C a diadduct $\text{NiO}_2(\text{CNBu}')_2(\text{CNCH}_3)_2$ can be isolated which loses one *tert*-butyl isocyanide at 3°C , giving $\text{NiO}_2(\text{CNBu}')(\text{CNCH}_3)_2$.

In solution $\text{Ni}(\text{CNBu}')_2\text{O}_2$ decomposes to $\text{Bu}'\text{NCO}$ and a material suggested to be $[\text{Ni}(\text{Bu}'\text{NCO})]_x$, which reacts with additional ligand to give NiL_4 . The oxygen complex also reacts with triphenylphosphine (yielding Ph_3PO and $\text{Ni}(\text{CNBu}')_2(\text{PPh}_3)_2$) and with tetracyanoethylene to give $\text{Ni}(\text{CNBu}')_2(\text{TCNE})$ and O_2 .

The oxidation of isocyanides to isocyanates with oxygen, catalyzed by $\text{Ni}(\text{CNR})_4$ or $\text{Ni}(\text{C}_8\text{H}_{12})_2$, has been known for some time (106). One can now postulate on the basis of these data that catalysis is being accomplished via oxygen coordination to the metal.

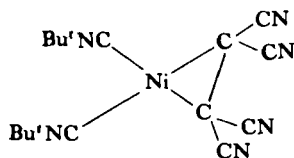
The infrared spectra of these oxygen compounds of nickel and palladium, and of oxygen complexes of rhodium $[\text{RhX}(\text{PPh}_3)_2(\text{RNC})\text{O}_2]$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$; $\text{R} = \text{C}_6\text{H}_{11}, p\text{-tolyl}, \text{Bu}'$] are also reported (67, 102). Oxygen-18 enrichment allowed definite assignments of some of the bands in these spectra.

A number of other ligand groups are found to add to $[\text{Ni}(\text{CNBu}')_2]_x$, including azobenzene, tetracyanoethylene, fumaronitrile, and maleonitrile, diphenylacetylene and dimethyl acetylenedicarboxylate (109, 110) [Eq. (29)].

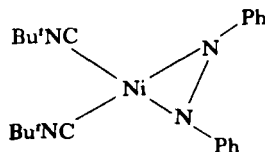


(L = PhN=NPh, PhC≡CPh, CH₃OCOC≡CCOOCH₃, TCNE, NCCH=CHCN)

Crystal structure determinations have been carried out for the tetracyanoethylene (139), azobenzene (52) and diphenylacetylene (52a) complexes, with molecular structures (XXXII) and (XXXIII). These complexes may



(XXXII)



(XXXIII)

be viewed as nickel(II) square-planar species. However, in the former the plane defined by the nickel and the two TCNE carbon atoms is skewed from the Ni(CNR)₂ plane by about 24°. The C=C bond length in the TCNE ligand is 1.476 Å, which may be compared to 1.339 Å for the free ligand and 1.506 Å in the complex IrBr(CO)(PPh₃)₂·TCNE. The nickel(isocyanide)–carbon distance is 1.866 Å. This is longer than the nickel–isocyanide distance in Ni(CNBu^t)₂N₂(C₆H₅)₂, found to be 1.840 Å. From this one can infer that there is more extensive back-donation to the isocyanide ligand in the azobenzene complex.

The fact that a number of M(CNBu^t)₂L complexes are known invites a comparison of their infrared spectra, particularly with respect to ν_{C≡N}. Table VI summarizes these data (110). One can see two infrared-active

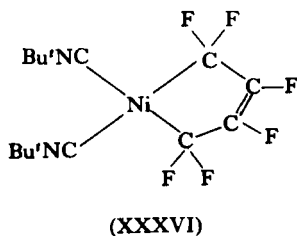
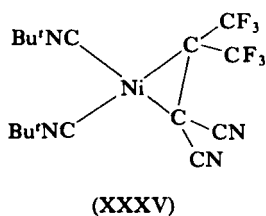
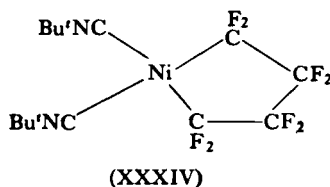
TABLE VI
INFRARED DATA ON Ni(CNBu^t)₂L

L	ν _{C≡N} (cm ⁻¹)
O ₂	2196, 2178
TCNE	2194, 2179
C ₆ H ₅ N=NC ₆ H ₅	2168, 2140
Fumaronitrile	2162, 2138
Maleic anhydride	2159, 2118
Dimethyl maleate	2154, 2120
CH ₃ OCOC≡CCOOCH ₃	2160, 2123

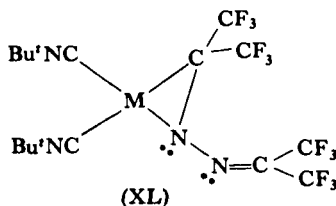
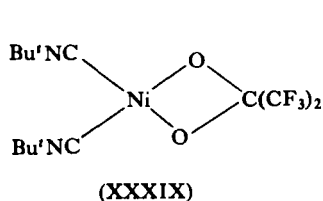
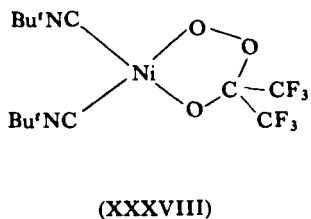
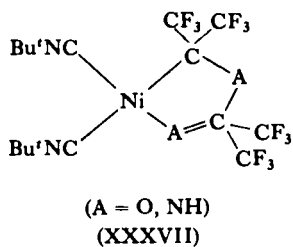
absorptions appropriate to the C_{2v} symmetry of these systems. There is a trend in ν_{CN} , presumably reflecting increasing π -donation to the ligand (L) in the series. Otsuka *et al.* (110) makes a point of the correlation of the ν_{CN} values and the electron affinities of the various ligands. They also observe that there is a similar trend in the differences in positions of the two infrared bands ($\Delta\nu_{a-b}$), which increases with the lower electron affinity of the ligand, and suggest that $\Delta\nu_{a-b}$ may be a good measure of effective backbonding of the ligand L.

A few $Ni(CNBu^t)_2L_2$ complexes are also observed (L = maleic anhydride, CO).

Stone *et al.* (43, 60, 61) have studied reactions of nickel and palladium isocyanides and a number of fluorocarbons which give a remarkable variety of products. With $Ni(CNBu^t)_4$ and fluoroolefins [C_2F_4 , $(CF_3)_2C=C(CN)_2$ and $CF_2=CFCF=CF_2$] the metallocyclic complexes (XXXIV), (XXXV), and (XXXVI) are observed (60, 61); the complex $Ni(CNBu^t)_2(C_3F_6)$, analo-



gous to (XXXV), is obtained with perfluoropropene. Using hexafluoroacetone or hexafluoroacetoneimine $(CF_3)_2C=A$ ($A=O, NH$), reaction occurs with incorporation of two fluorocarbon units in a heterocyclic ring, giving (XXXVII). The reaction is presumed to occur stepwise. Evidence to support this comes from the reaction of hexafluoroacetone (HFA) and

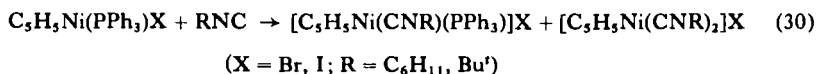


$\text{Ni}(\text{CNBu}')_2\text{HFA}$ [the latter species obtained in a two-step reaction: (1) $(\text{COD})_2\text{Ni} + \text{HFA} \rightarrow (\text{COD})\text{NiHFA}$; (2) $(\text{COD})\text{NiHFA} + 2\text{CNBu}' \rightarrow \text{Ni}(\text{CNBu}')_2\text{HFA}$] which yields the same product.

The reaction of $(\text{Bu}'\text{NC})_2\text{NiO}_2$ and hexafluoroacetone at -50°C yields a cyclic peroxo complex (XXXVIII) which loses one oxygen on dissolution in ether to give (XXXIX).

The reaction of bis(trifluoromethyl)diazomethane with either $\text{Ni}(\text{CNBu}')_4$ or $[\text{Pd}(\text{CNR})_2]_x$ ($\text{R} = \text{Bu}', \text{Cy}$), also gave interesting complexes (XL); the structure of an analogous species, $\text{Pt}(\text{PPh}_3)_2(\text{CF}_3)_4\text{C}_2\text{N}_2$, was determined by X-ray crystallography (43).

A few cyclopentadienylnickel isocyanide complexes (163, 164) have been reported, arising in the following reactions:

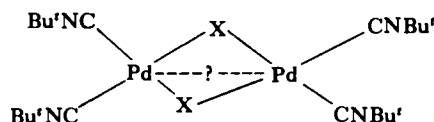


Mention was made earlier about insertion reactions into nickel alkyl bonds (108, 164), and about polymerizations of olefins by isocyanide nickel complexes (31, 174).

A large amount of the work on palladium isocyanide complexes has been mentioned earlier, in discussions on insertion reactions (30, 74, 108, 169, 170) and on addition reactions of coordinated isocyanides (25, 33, 34, 49); the reactions of $[\text{Pd}(\text{CNBu}')_2]_x$ with oxygen (107) and with various olefins (29, 110) were noted.

In addition, there has been a general elaboration on the syntheses of palladium(II) complexes. Foremost, one might mention the syntheses of various SnCl_3 and GeCl_3 complexes. Treatment of $\text{Pd}(\text{CNR})_2\text{Cl}_2$ ($\text{R} = \text{C}_6\text{H}_{11}$, $p\text{-C}_6\text{H}_4\text{NO}_2$) with either $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ or CsGeCl_3 affords $\text{Pd}(\text{CNR})_2(\text{MCl}_3)_2$ species ($\text{M} = \text{Ge}, \text{Sn}$) (47). From $\text{Pd}(\text{CNC}_6\text{H}_5)\text{LCl}_2$ ($\text{L} = \text{PPh}_3$) and CsGeCl_3 one may get either $\text{Pd}(\text{CNC}_6\text{H}_5)\text{L}(\text{GeCl}_3)\text{Cl}$ or $\text{Pd}(\text{CNC}_6\text{H}_5)\text{L}(\text{GeCl}_3)_2$, depending on the molar ratio of the reactants (47). In the analogous reaction with SnCl_2 the two SnCl_3 compounds are formed (25). The MX_3 groups may be cleaved with halogens (Cl_2 , I_2).

One of the more interesting reports on palladium isocyanides discusses the formation of a palladium(I) complex (111). The reaction of $[\text{Pd}(\text{CNBu}')_2]_x$ and $\text{Pd}(\text{CNBu}')_2\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) in chlorobenzene at -30°C gives the yellow crystalline complexes $[\text{Pd}(\text{CNBu}')_2\text{X}]_2$; the crystals are reasonably stable in air and are also thermally stable. The complexes are diamagnetic, and the presence of terminal ν_{CN} but not of bridging ν_{CN} in the infrared spectra is noted; the infrared spectra also suggest bridging halogens. These workers suggest structure (XLI) for these compounds. They propose



(XLI)

that the observed diamagnetism arises by a strong magnetic interaction between the metals either through space or through the bridging halogens. Though the possibility of a metal-metal bond is not mentioned, this also seems like a reasonable alternative.

It is possible to replace one isocyanide by triphenylphosphine, or to replace two isocyanides with diphos, giving phosphine analogues of these complexes. These species are not available from analogous reactions of phosphine-palladium(0) and (II) complexes. Reactions with active alkyl halides proceeds with oxidation; nitric oxide also oxidizes these complexes. [Eqs. (31, 32)].



Most work on platinum involves complexes in the divalent state. Malatesta and Bonati report no platinum(0) or platinum(IV) species. The lack of

isocyanide complexes of platinum in the higher oxidation state is probably expected, as isocyanide complexes involving high oxidation states for metals are at best rare. However, there are lower oxidation state isocyanide complexes of both nickel and palladium, as mentioned above, and one might expect such species for platinum as well. One might anticipate their somewhat low stability, however, as the trend in stability among these species (and also among the carbonyls) is $\text{Ni} > \text{Pd} > \text{Pt}$.

There is now one report on platinum(0) isocyanide complexes (85). When $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ is treated with CNBu^t in *n*-pentane at -20°C , a compound, $\text{Pt}(\text{PPh}_3)_2(\text{CNBu}^t)_2$, is obtained. This material has a ν_{CN} frequency at 2030 cm^{-1} , indicative of the extensive π -donation to the ligand. It decomposes slowly in air. With CO one isocyanide is displaced. Oxidative addition reactions occur readily with I_2 , CH_3I , and CF_3I , and Ph_3SnCl . From the first three reactions five-coordinate species $[\text{Pt}(\text{PPh}_3)_2(\text{CNBu}^t)_2\text{-R}]\text{I}$ ($\text{R} = \text{I}, \text{CH}_3, \text{CF}_3$) are obtained, the proposed structure being assigned by analyses and conductivity data (each is a 1:1 electrolyte). The tin complex, $\text{Pt}(\text{PPh}_3)_2(\text{CNBu}^t)_2(\text{SnPh}_3)\text{Cl}$ has a low conductivity value.

Platinum(II) isocyanide complexes of the general formulas $[\text{PtL}_4]^{2+}$, $[\text{PtL}_3\text{X}]^+$, and PtL_2X_2 and substituted derivatives thereof ($\text{L} = \text{RNC}$, $\text{X} = \text{halogen}, \text{H}, \text{R}, \text{etc.}$), have been studied recently and will be the main subjects of discussion. It may be observed that much work on complexes of the first and third molecular stoichiometries had been reported previously.

Complexes of the formula $[\text{Pt}(\text{CNR})_4]\text{PtCl}_4$ ($\text{R} = \text{C}_6\text{H}_5$, *p*-tolyl, *p*- $\text{C}_6\text{H}_4\text{OCH}_3$, C_6H_{11}) are obtained from K_2PtCl_4 and the isocyanide in aqueous media (27); they join a number of other such complexes, previously known, which were formed in the same manner (90). These complexes may be either blue and organic-insoluble (C_6H_5 , *p*-tolyl), or red and organic-soluble (C_6H_{11} , *p*- $\text{C}_6\text{H}_4\text{OCH}_3$). There are structural differences in these two types of complexes; the former are presumed to have strong axial metal-metal interactions. Refluxing in chloroform converts these ionic complexes to *cis*- $\text{Pt}(\text{CNR})_2\text{Cl}_2$ species. Another method for synthesis of $[\text{PtL}_4]^{2+}$ complexes utilizes the alkylation of the tetracyanoplatinate(II) anion with a strong alkylating agent such as $[(\text{CH}_3)_3\text{O}]\text{BF}_4$ (147); the alkylation reaction with methyl iodide or methyl sulfate, studied many years ago, gives only $\text{Pt}(\text{CNR})_2(\text{CN})_2$ (90). Alkylation of $\text{Pt}(\text{PPh}_3)_2(\text{CN})_2$ with $[(\text{CH}_3)_3\text{O}]\text{BF}_4$, disubstitution of $[\text{Pt}(\text{CNCH}_3)_4]^{2+}$ with various phosphines (147), and substitution of chloride ion in the complex $\text{Pt}(\text{PPhMe}_2)_2\text{Cl}_2$ by isocyanide in the presence of NaPF_6 (42) all give rise to the phosphine-

substituted derivatives $[\text{Pt}(\text{phos})_2(\text{CNR})_2]^{2+}$. The latter reaction is interesting in that most reactions of this type have given $[\text{Pt}(\text{phos})_2(\text{CNR})\text{X}]^+$ species (38, 39).

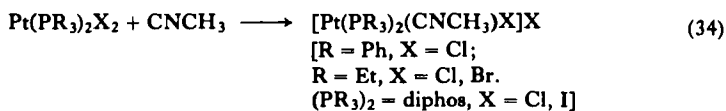
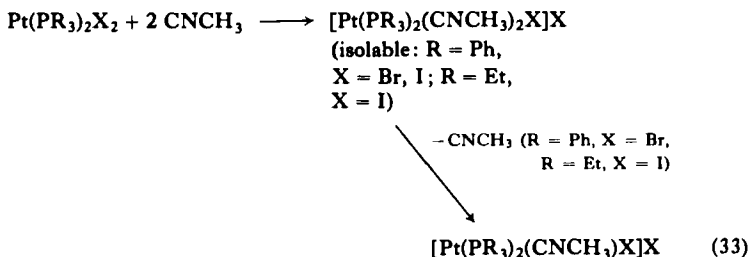
An extensive collection of $[\text{PtL}_2(\text{CNR})\text{X}]^+$ complexes have been reported. Church and Mays (38, 39) describe reactions of $\text{Pt}(\text{L}_2)\text{RX}$ with isocyanides (and with other ligands), in the presence of a halogen acceptor such as NaClO_4 or NaPF_6 . The latter species is apparently important to this reaction; the driving force is associated with the precipitation of NaX from the reaction system. The following complexes are reported: *trans*- $[\text{Pt}(\text{PEt}_3)_2(\text{CNR})\text{R}']\text{ClO}_4$ (38) ($\text{R} = \text{Bu}'$, $p\text{-C}_6\text{H}_4\text{OCH}_3$, $\text{R}' = p\text{-C}_6\text{H}_4\text{F}$, H , Br , Cl); *trans*- $[\text{Pt}(\text{AsEt}_3)_2(\text{CNBu}')\text{R}']\text{ClO}_4$ ($\text{R}' = \text{H}$, Cl). Several correlations within related series of compounds were observed. For example, in the arsine complexes, for $\text{R}' = \text{chlorine}$, the value of $\nu_{\text{Cl-Pt}}$ shifts regularly as a function of the trans ligand donor ability, $\text{PEt}_3 > \text{AsEt}_3 > \text{P}(\text{OMe})_3 > \text{P}(\text{OPh})_3 > \text{CNAr} > \text{CNR} > \text{CO}$.

Treichel, Knebel, and Hess (147) present a detailed study of reactions of methyl isocyanide with $\text{Pt}(\text{PPh}_3)_2\text{X}_2$ ($\text{X} = \text{Cl}$, Br , I) and $\text{Pt}(\text{PEt}_3)_2\text{Cl}_2$. They observe that these reactions generally lead to ionic products, arising from displacement of a halide ion by the isocyanide. This observation is somewhat unusual, as many previous instances have been cited where the equilibrium established between L_2PtX_2 , L' , and $[\text{L}_2\text{PtL}'\text{X}]\text{X}$ generally favor the reactants [Eq. (32)]. This has generally meant that the isolation of the ionic

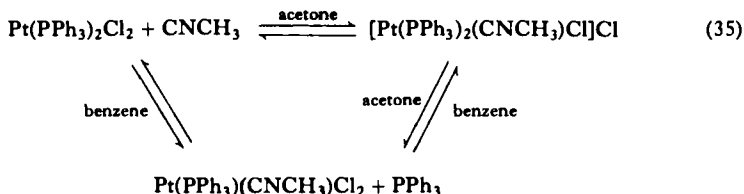


species from this reaction has been impossible, unless of course there is a halide acceptor present; this is the route used by Church and Mays, described above. The only major exception to this generalization was also observed using methyl isocyanide; from $\text{Pt}(\text{PPh}_3)_2\text{RX}$ and CNCH_3 , ionic complexes $[\text{Pt}(\text{PPh}_3)_2(\text{CNCH}_3)\text{R}]\text{X}$ were reported (144).

The products obtained from the $\text{Pt}(\text{PR}_3)_2\text{X}_2\text{-CNCH}_3$ reactions were dependent on the nature of the platinum species. Five-coordinate adducts, $[\text{Pt}(\text{PR}_3)_2(\text{CNCH}_3)_2\text{X}]\text{X}$, were isolated for the iodo and bromo complexes ($\text{R} = \text{Ph}$), although the latter was unstable and slowly lost isocyanide. The observation of five-coordination here is somewhat unusual, but since this report, it was also observed in a different situation (85), mentioned above. The more common observation was the isolation of four-coordinate species, implying the low stability of most five-coordinate complexes. Data on these reactions are summarized below [Eqs. (33, 34)].

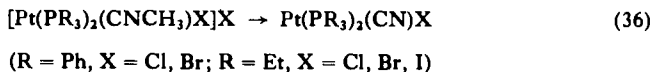


The reaction of $\text{Pt}(\text{PPh}_3)_2\text{Cl}_2$ and CNCH_3 was unusual in that it was solvent-dependent, giving $[\text{Pt}(\text{PPh}_3)_2(\text{CNCH}_3)\text{Cl}]\text{Cl}$ in acetone, and $\text{Pt}(\text{PPh}_3)(\text{CNCH}_3)\text{Cl}_2$ in benzene. A simple interconversion between these complexes is possible, dependent on solvent choice [Eq. (35)].



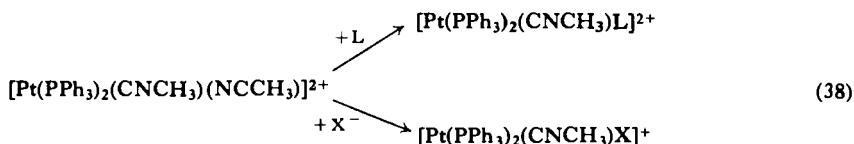
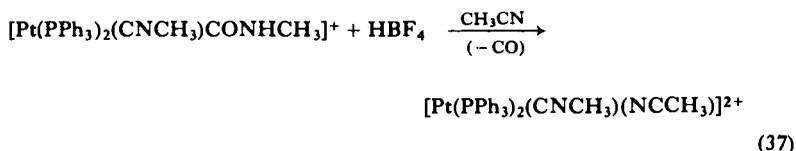
Treichel, Knebel, and Hess provided further data on these systems by studying reactions of $[\text{Pt}(\text{PR}_3)_2(\text{CNCH}_3)_2]^{2+}$ with various halide ions and with pseudohalides. A series of five-coordinate complexes were obtained from reactions with iodide ion ($\text{PR}_3 = \text{PPh}_3, \text{PPh}_2\text{Me}, \text{PPhMe}_2, \text{PEt}_3$), and a study was carried out to measure the stability of these complexes with respect to ligand loss (155). Stability constants for several of these complexes were obtained from spectroscopic data. Other reactants (Cl, Br, CN, SCN) generally yielded the appropriate $[\text{Pt}(\text{PR}_3)_2(\text{CNCH}_3)\text{X}]^+$ species, as expected.

During a study of these complexes, Treichel and Hess (145, 147) heated $[\text{Pt}(\text{PPh}_3)_2(\text{CNCH}_3)\text{Cl}]\text{Cl}$, expecting to obtain $\text{Pt}(\text{PPh}_3)(\text{CNCH}_3)\text{Cl}_2$; instead a novel dealkylation reaction occurred. This was extended to other related species [Eq. (36)]. Remarkably, very few examples of such reactions



had been previously observed. There is one historical reference (90); and Treichel *et al.* have also observed this type of reaction in studies of the $\text{C}_6\text{F}_5\text{Li}[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CNCH}_3]^+$ (143), and $\text{Pt}(\text{PPh}_3)_2(\text{C}_6\text{F}_5)\text{Br}-\text{CNCH}_3$ (144) reaction systems.

The novel reaction of hydroxide ion with $\text{Pt}(\text{PPh}_3)_2(\text{CNCH}_3)_2^{2+}$ to give $[\text{Pt}(\text{PPh}_3)_2(\text{CNCH}_3)(\text{CONHCH}_3)]^+$ and the analogous SH^- and NHR^- additions (84, 149, 150) were discussed above. This carboxamido complex was a useful precursor in syntheses of a number of new complexes, by the following reaction sequences [Eqs. (37, 38)].



($\text{L} = \text{PPh}_3, \text{PEt}_3, \text{py}, \text{S}(\text{CH}_3)_2, \text{N}(\text{CH}_3)_3, \text{CNCH}_3$;

$\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{SCN}, \text{CN}, \text{NO}_2, \text{OH}$)

Two other references to $[\text{PtL}_2(\text{CNR})\text{R}']^+$ complexes are the nonreaction of $[\text{Pt}(\text{PPhEt}_2)_2(\text{CNC}_6\text{H}_4\text{CH}_3)\text{H}]^+$ with ethylene (41) [in contrast to the addition of ethylene to $\text{Pt}(\text{PEt}_3)_2\text{HCl}$ to give $\text{Pt}(\text{PEt}_3)_2(\text{Et})\text{Cl}$] and the insertion of InCl into the platinum chloride bond in $[\text{Pt}(\text{PEt}_3)_2(\text{CNC}_6\text{H}_4\text{OCH}_3)\text{Cl}]^+$ giving $[\text{Pt}(\text{PEt}_3)_2(\text{CNC}_6\text{H}_4\text{OCH}_3)\text{InCl}_2]^+$ (68).

The preparation of several complexes of the general formula $[\text{L}_4\text{Pt}_2\text{X}_2]^{2+}$ ($\text{L} = \text{phos}, \text{CNCH}_3$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) from reactions of L_2PtX_2 and $[(\text{CH}_3)_3\text{O}]\text{BF}_4$ was noted (151). In this reaction the oxonium salt serves as a halogen acceptor, yielding CH_3X and $(\text{CH}_3)_2\text{O}$; this is a not generally observed mode of reaction for this species. The new complex $\text{Pt}(\text{CNCH}_3)_2(\text{CH}_3)\text{I}$, obtained from $\text{Pt}(\text{CNCH}_3)_2\text{Cl}_2$ and CH_3MgI , is also noted (153), as are several trichlorostannato complexes $\text{Pt}(\text{CNR})_2(\text{SnCl}_3)_2$ ($\text{R} = \text{Ph}, p\text{-tolyl}, \text{C}_6\text{H}_{11}, p\text{-C}_6\text{H}_4\text{OCH}_3$) (27) and $\text{Pt}(\text{PPh}_3)(\text{CNR})(\text{SnCl}_3)_2$ ($\text{R}' =$

C_6H_{11} , *p*-tolyl, *p*- $C_6H_4NO_2$) (25) obtained from $Pt(CNR)_2Cl_2$ or $Pt(PPh_3)(CNR')Cl_2$ and stannous chloride.

Insertion reactions of platinum(II) alkyl and aryl complexes (144, 153, 171), nucleophilic displacement of isocyanide from $[Pt(PR_3)_2(CNCH_3)_2]^{2+}$ (147) and additions of alcohols and related substances to isocyanides bonded to platinum (8, 9, 25, 33, 34, 100, 117) were discussed earlier.

F. Other Metals

There are scattered reports on isocyanide complexes of other metals including copper and gold, vanadium, and several lanthanides and actinides.

The complex $C_5H_5V(CO)_3CNH$ arises from protonation of $[C_5H_5V(CO)_3CN]^-$ (56). This is the only vanadium isocyanide complex known.

There is an interesting report (141) on copper(II) isocyanide complexes, $[Cu(CNBU')_4(H_2O)_2]X_2$ ($X = ClO_4$ or BF_4). As might be expected these complexes are quite unstable with respect to metal reduction; they readily decompose to $[Cu(CNBU')_4]X$ complexes. There is a report on $C_5H_5Cu(CNCH_3)$ described as a white complex obtained in 57% yield from $(CH_3NCCuI)_4$ and C_5H_5TI (45). This species is air-sensitive and thermally unstable, decomposing in several minutes at room temperature. It is more stable than the corresponding carbonyl, however. The infrared spectrum shows a ν_{CN} at 2190 cm^{-1} vs. 2158 cm^{-1} for the free isocyanide; this indicates little π -bonding to this ligand.

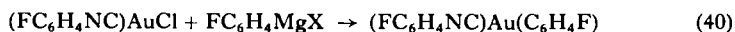
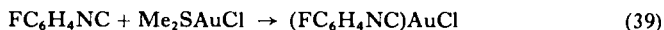
The analogous complex $C_5H_5Cu(CNBU')$ is obtained from Cu_2O , $CNBU'$, and C_5H_6 (132). The reaction with indene gave a complex of different stoichiometry, however. This complex, $C_9H_7Cu(CNBU')_3$, is suggested to be a fluxional monohapto or pentahapto species by virtue of its PMR spectrum. The cyclopentadienyl complex is a catalyst for fulvene formation from cyclopentadiene and ketones or aldehydes. The catalytic activity is enhanced by the presence of additional isocyanide (132).

The colorless, diamagnetic copper(I) complex $Cu(acac)(CNPh)_2$ is formed from copper(I) acetylacetonate and phenyl isocyanide (103). The copper(I) complex $(CuCl)_2(CNC_6H_{11})_2pip$ was isolated (124); it decomposes to $C_5H_{10}NCH=NC_6H_{11}$. Primarily on this basis, copper(I) complexes are presumed to be intermediates in various α -addition reactions to isocyanides (Section III,D).

Beck and Fehlhammer (18, 19) describe reactions of several metal azide complexes, including $Au(N_3)_4^-$, with isocyanides which yielded a tetrakis-(tetrazolato)aurate(I) species. The formation of $Au(PPh_3)C(OCH_3)=N-p$ -

tolyl from $\text{Au}(\text{PPh}_3)\text{Cl}$, *p*-tolylNC, and KOH in methanol was noted (100).

The complexes *m*- and *p*-($\text{FC}_6\text{H}_4\text{NC}$)AuCl and *m*- and *p*-($\text{FC}_6\text{H}_4\text{NC}$)-Au($\text{C}_6\text{H}_4\text{F}$) were prepared (158) in the following reactions [Eqs. (39, 40)]:



Inductive and resonance parameters, σ_R^0 , σ_I , were evaluated for the isocyanide ligand from ^{19}F chemical shifts; they suggest that the isocyanide is a good σ -donor and a weak π -acceptor.

There are reports of several uranium isocyanide complexes. Fischer *et al.* (57) prepared $\text{U}(\text{C}_5\text{H}_5)_3$ from uranium metal and $\text{U}(\text{C}_5\text{H}_5)_4$; this adds THF to give an isolable complex. The THF can be displaced by cyclohexyl isocyanide to give $\text{U}(\text{C}_5\text{H}_5)_3\text{CNC}_6\text{H}_{11}$. This complex shows ν_{CN} at 2160 cm^{-1} vs. 2130 for the free ligand. The complex, $\text{U}(\text{CNC}_6\text{H}_{11})_4\text{I}_4$, a very moisture-sensitive and thermally unstable complex, is formed from the isocyanide and UI_4 (87). The value of ν_{CN} in this species is 2190 cm^{-1} . Other isocyanide complexes of ThI_4 , UBr_4 , UCl_4 , and UO_2Cl are mentioned also.

The PMRs of several triscyclopentadienyl-lanthanide metal complexes of cyclohexyl isocyanide $(\text{C}_5\text{H}_5)_3\text{MCNC}_6\text{H}_{11}$ ($\text{M} = \text{Pr, Nd, Ho, Tm, Yb}$) are reported (159, 160).

REFERENCES

1. Ablov, A. V., Batyr, D. G., and Sarysh, M. P., *Zh. Neorg. Khim.* **13**, 3393 (1968).
2. Ablov, A. V., Batyr, D. G., and Sarysh, M. P., *Zh. Neorg. Khim.* **14**, 2887 (1969).
- 2a. Alper, H., and Partis, R. A., *J. Organometal. Chem.* **35**, C40 (1972).
3. Angelici, R. J., private communication.
4. Angelici, R. J., and Ingemanson, C. M., *Inorg. Chem.* **8**, 83 (1969).
5. Angelici, R. J., and Charley, L. M., *J. Organometal. Chem.* **24**, 205 (1970).
6. Araneo, A., Bonati, F., and Minghetti, G., *J. Organometal. Chem.* **25**, C25 (1970).
7. Aumann, R., and Fischer, E. O., *Chem. Ber.* **101**, 954 (1968); communication, *Angew. Chem., Int. Ed. Engl.* **6**, 879 (1967).
8. Badley, E. M., Chatt, J., Richards, R. L., and Sim, G. A., *J. Chem. Soc., D* 1322 (1969).
9. Badley, E. M., Chatt, J., and Richards, R. L., *J. Chem. Soc., A* 21 (1971).
10. Badley, E. M., D.Phil. Thesis, Univ. of Sussex (1969). Quoted in Badley *et al.* (9).
11. Balch, A. L., and Miller, J., *J. Organometal. Chem.* **32**, 263 (1971).
12. Bamford, C. H., Eastmond, G. C., and Hargreaves, K., *Trans. Faraday Soc.* **64**, 1611 (1968).
13. Bancroft, G. M., Mays, M. J., and Prater, B. E., *Chem. Commun.* 1374 (1968).
14. Bancroft, G. M., Mays, M. J., and Prater, B. E., *J. Chem. Soc., D* 39 (1969).
15. Bancroft, G. M., Mays, M. J., and Prater, B. E., *Discuss. Faraday Soc.* 136 (1969).

16. Bancroft, G. M., Mays, M. J., and Prater, B. E., *J. Chem. Soc., A* 956 (1970).
17. Bancroft, G. M., Garrod, R. E. B., Maddock, A. G., Mays, M. J., and Prater, B. E., *J. Chem. Soc., D* 200 (1970).
18. Beck, W., and Fehlhammer, W. P., *Angew. Chem., Int. Ed. Engl.* **6**, 169 (1967).
19. Beck, W., Burger, K., and Fehlhammer, W. P., *Chem. Ber.* **104**, 1816 (1971).
20. Benedict, J. J., Ph.D. Thesis, Univ. of Wisconsin (1971).
21. Berrett, R. R., Fitzsimmons, B. W., Gans, P., Irving, H. M. N. H., and Stratton, P., *J. Chem. Soc., A* 904 (1969).
22. Bolton, E. S., Dekker, M., Knox, G. R., and Robertson, C. G., *Chem. Ind. (London)* 327 (1969).
23. Bonati, F., and Minghetti, G., *Inorg. Chem.* **9**, 2642 (1970).
24. Bonati, F., and Minghetti, G., *J. Organometal. Chem.* **22**, 195 (1970).
25. Bonati, F., Minghetti, G., Boschi, T., and Crociani, B., *J. Organometal. Chem.* **25**, 255 (1970).
26. Bonati, F., Minghetti, G., and Leoni, R., *J. Organometal. Chem.* **25**, 223 (1970).
27. Bonati, F., and Minghetti, G., *J. Organometal. Chem.* **24**, 251 (1970).
28. Boorman, P. M., Craig, P. J., and Swaddle, T. W., *Can. J. Chem.* **48**, 838 (1970).
29. Boschi, T., Uguagliati, P., and Crociani, B., *J. Organometal. Chem.* **30**, 283 (1971).
30. Boschi, T., and Crociani, B., *Inorg. Chim. Acta* **5**, 477 (1971).
31. Breil, H., and Wilke, G., *Angew. Chem., Int. Ed. Engl.* **9**, 367 (1970).
32. Brunner, H., and Schindler, H. D., *J. Organometal. Chem.* **19**, 135 (1969).
33. Burke, A., Balch, A. L., and Enemark, J. H., *J. Amer. Chem. Soc.* **92**, 2555 (1970).
34. Butler, W. M., and Enemark, J. H., *Inorg. Chem.* **10**, 2416 (1971).
35. Caulton, K. G., and Fenske, R. F., *Inorg. Chem.* **7**, 1273 (1968).
36. Chatt, J., Melville, D. P., and Richards, R. L., *J. Chem. Soc., A* 1169 (1971).
37. Christian, D. F., and Roper, W. R., *J. Chem. Soc., D* 1271 (1971).
38. Church, M. J., and Mays, M. J., *J. Chem. Soc., A* 3074 (1968); communication, *Chem. Commun.* 435 (1968).
39. Church, M. J., and Mays, M. J., *J. Chem. Soc., A* 1938 (1970).
40. Clark, H. C., Dixon, K. R., and Jacobs, W. J., *J. Amer. Chem. Soc.* **91**, 1346 (1969).
41. Clark, H. C., and Kierosawa, H., *J. Chem. Soc., D* 957 (1971).
42. Clark, H. C., and Manzer, L. E., *J. Organometal. Chem.* **30**, C89 (1971).
43. Clemens, J., Davis, R. E., Green, M., Oliver, J. D., and Stone, F. G. A., *J. Chem. Soc., D* 1095 (1971).
44. Connor, J. A., and Jones, E. M., *J. Chem. Soc., D* 570 (1971).
45. Cotton, F. A., and Marks, T. J., *J. Amer. Chem. Soc.* **92**, 5114 (1970).
46. Crociani, B., and Boschi, T., *J. Organometal. Chem.* **24**, C1 (1970).
47. Crociani, B., Boschi, T., and Nicolini, M., *Inorg. Chim. Acta* **4**, 577 (1970).
48. Crociani, B., Boschi, T., and Belluco, U., *Inorg. Chem.* **9**, 2021 (1970).
49. Crociani, B., Nicolini, M., and Boschi, T., *J. Organometal. Chem.* **33**, C81 (1971).
50. Dart, J. W., Lloyd, M. K., McCleverty, J. A., and Mason, R., *J. Chem. Soc., D* 1197 (1971).
51. Dartiguenave, Y., Dartiguenave, M., and Gray, H. B., *Bull. Soc. Chim. Fr.* 4225 (1969).
52. Dickson, R. S., Ibers, J. A., Otsuka, S., and Tatsuno, Y., *J. Amer. Chem. Soc.* **93**, 4636 (1971); Dickson, R. S., and Ibers, J. A., *ibid.* **94**, 2988 (1972).
- 52a. Dickson, R. S., and Ibers, J. A., *J. Organometal. Chem.* **36**, 191 (1972).
53. Distefano, G., Innorta, G., Pignataro, S., and Foffani, A., *J. Organometal. Chem.* **14**, 165 (1968).
54. Enemark, J. H., private communication.
55. Fantucci, P. C., Valenti, V., and Cariati, F., *Inorg. Chim. Acta* **5**, 425 (1971).

56. Fischer, E. O., and Schneider, R. J. J., *J. Organometal. Chem.* **12**, P27 (1968).
57. Fischer, E. O., Kanellakopulos, B., Dornberger, E., and Baumgärtner, F., *J. Organometal. Chem.* **24**, 507 (1970).
58. Gilmore, C. J., Watkins, S. F., and Woodward, P., *J. Chem. Soc., A* 2833 (1969).
59. Greatrex, R., Greenwood, N. N., Rhee, I., Ryang, M., and Tsutsumi, S., *J. Chem. Soc., D* 1193 (1970).
60. Greco, A., Green, M., Shakshooki, S. K., and Stone, F. G. A., *J. Chem. Soc., D* 1374 (1970).
61. Green, M., Shakshooki, S. K., and Stone, F. G. A., *J. Chem. Soc., A* 2828 (1971).
62. Green, M. L. H., and Lindsell, W. E., *J. Chem. Soc., A* 2150 (1969).
63. Guttenberger, J. F., Strohmeier, W., and Mueller, F. J., *Z. Naturforsch., B* **22**, 1091 (1967).
64. Haas, H., and Sheline, R. K., *J. Chem. Phys.* **47**, 2996 (1967).
65. Hall, D., Slater, J. H., Fitzsimmons, B. W., and Wade, K., *J. Chem. Soc., A* 800 (1971).
66. Herlinger, A. W., and Brown, T. L., *J. Amer. Chem. Soc.*, **93**, 1791 (1971).
67. Hiroto, K., Yamamoto, M., Otsuka, S., Nakamoto, A., and Tatsuno, Y., *Chem. Commun.* 533 (1968).
68. Hsieh, A. T. T., and Mays, M. J., *Inorg. Nucl. Chem. Lett.* **7**, 223 (1971).
69. Johnston, R. D., Basolo, F., and Pearson, R. G., *Inorg. Chem.* **10**, 247 (1971).
70. Joshi, K. K., Pauson, P. L., and Stubbs, W. H., *J. Organometal. Chem.* **1**, 51 (1963).
71. Joshi, K. K., Mills, O. S., Pauson, P. L., Shaw, B. W., and Stubbs, W. H., *Chem. Commun.* 181 (1965).
72. Innorta, G., Distefano, G., and Pignataro, S., *Int. J. Mass. Spectrom. Ion Phys.* **1**, 435 (1968).
73. Jovanovic, B., Manojlovic-Muir, L., and Muir, K. W., *J. Organometal. Chem.* **33**, C75 (1971).
74. Kajimoto, T., Takahashi, H., and Tsuji, J., *J. Organometal. Chem.* **23**, 275 (1970).
75. Kaska, W. C., and Kimball, M. E., *Inorg. Nucl. Chem. Lett.* **4**, 719 (1968).
76. Kataoka, N., and Kon, H., *J. Amer. Chem. Soc.* **90**, 2978 (1968).
77. Kataoka, N., and Kon, H., *J. Phys. Chem.* **73**, 803 (1969).
78. Keith, R. E., Scott, J. L., and Crook, J. R., *Abstr. 161st Nat. Meeting, Amer. Chem. Soc.* INOR. 21 (1971).
79. Kelly, M., Postgate, J. R., and Richards, R. L., *Biochem. J.* **102**, 1 (1967).
80. Kelly, M., *Biochem. J.* **107**, 1 (1968).
81. Kimball, M. E., Pratt, D. W., and Kaska, W. C., *Inorg. Chem.* **7**, 2006 (1968).
82. King, R. B., and Efraty, A., *J. Amer. Chem. Soc.* **93**, 564 (1971).
83. King, R. B., and Pannell, K. H., *J. Amer. Chem. Soc.* **90**, 3984 (1968).
84. Knebel, W. J., and Treichel, P. M., *J. Chem. Soc., D* 516 (1971).
- 84a. Lappert, M. F., and Oliver, A. J., *J. Chem. Soc., D* 274 (1972).
85. Larkin, G. A., Mason, R., and Wallbridge, M. G. H., *J. Chem. Soc., D* 1054 (1971).
86. Lewis, D. F., and Lippard, S. J., *Inorg. Chem.* **11**, 621 (1972).
87. Lux, F., and Bufer, U. E., *Angew. Chem., Int. Ed. Engl.* **10**, 274 (1971).
88. Maher, J. P., *J. Chem. Soc., A* 2918 (1968).
89. Malatesta, L., Sacco, A., and Padoa, G., *Ann. Chim. (Rome)* **43**, 617 (1953).
90. Malatesta, L., and Bonati, F., "Isonitrile Complexes of Metals." Wiley, New York (1969).
91. Malathi, N., and Puri, S. P., *Chem. Phys. Lett.* **10**, 154 (1971).
92. Mann, B. E., Masters, C., and Shaw, B. L., *J. Chem. Soc., D* 847 (1970).
93. Mann, B. E., Masters, C., and Shaw, B. L., *J. Inorg. Nucl. Chem.* **33**, 2195 (1971).

94. Matteson, D. S., and Bailey, R. A., *J. Amer. Chem. Soc.* **90**, 3761 (1968).
95. Matteson, D. S., and Bailey, R. A., *J. Amer. Chem. Soc.* **91**, 1975 (1969); communication, *ibid.* **89**, 6389 (1967).
96. Mays, M. J., and Prater, B. E., *J. Chem. Soc., A* 2525 (1969).
97. McCleverty, J. A., and James, T. A., *J. Chem. Soc., A* 1596 (1971).
98. Meier, M., Basolo, F., and Pearson, R. G., *Inorg. Chem.* **8**, 795 (1969).
99. Miller, J., Balch, A. L., and Enemark, J. H., *J. Amer. Chem. Soc.* **93**, 4613 (1971).
100. Minghetti, G., and Bonati, F., *Atti. Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Natur., Rend.* **49**, 287 (1970).
101. Müller, J., and Herberhold, M., *J. Organometal. Chem.* **13**, 399 (1968).
102. Nakamura, A., Tatsuno, Y., Yamamoto, M., and Otsuka, S., *J. Amer. Chem. Soc.* **93**, 6052 (1971).
103. Nast, R., and Lepel, W. H., *Chem. Ber.* **102**, 3224 (1969).
104. Nast, R., and Schulz, H., *Chem. Ber.* **103**, 785 (1970).
105. Nast, R., Schulz, H., and Moerler, H. D., *Chem. Ber.* **103**, 777 (1970).
106. Otsuka, S., Nakamura, A., and Yoshida, T., *Chem. Commun.* 836 (1967).
107. Otsuka, S., Nakamura, A., and Tatsuno, Y., *J. Amer. Chem. Soc.* **91**, 6994 (1969).
108. Otsuka, S., Nakamura, A., and Yoshida, T., *J. Amer. Chem. Soc.* **91**, 7196 (1969).
109. Otsuka, S., Yoshida, T., and Tatsuno, Y., *J. Chem. Soc., D* 67 (1971).
110. Otsuka, S., Yoshida, T., and Tatsuno, Y., *J. Amer. Chem. Soc.* **93**, 6462 (1971).
111. Otsuka, S., Tatsuno, Y., and Ataka, K., *J. Amer. Chem. Soc.* **93**, 6705 (1971).
112. Pauson, P. L., and Stubbs, W. H., *Angew. Chem., Int. Ed. Engl.* **1**, 333 (1962).
113. Podoa, G., *Ann. Chim. (Rome)* **45**, 28 (1955).
114. Prater, B. E., *Inorg. Nucl. Chem. Lett.* **7**, 1071 (1971).
115. Prater, B. E., *J. Organometal. Chem.* **27**, C17 (1971); *ibid.* **34**, 379 (1972).
116. Prater, B. E., *J. Organometal. Chem.* **33**, 215 (1971).
117. Rouschias, G., and Shaw, B. L., *J. Chem. Soc., D* 183 (1970); *J. Chem. Soc., A* 2097 (1971).
118. Saegusa, T., Ito, Y., Kobayashi, S., and Hiroto, K., *J. Amer. Chem. Soc.* **89**, 2240 (1967).
119. Saegusa, T., Ito, Y., and Kobayashi, S., *Tetrahedron Lett.* 935 (1968).
- 119a. Saegusa, T., Ito, Y., Tomita, S., and Kinoshita, H., *Bull. Chem. Soc. Jap.* **45**, 496 (1972).
120. Saegusa, T., Kobayashi, S., Hirota, K., Okumura, Y., and Ito, Y., *Bull. Chem. Soc. Jap.* **41**, 1638 (1968).
121. Saegusa, T., Ito, Y., Kobayashi, S., and Tomita, S., *Chem. Commun.* 273 (1968).
122. Saegusa, T., and Ito, Y., *Yuki Gosei Kagaku Shi* **26**, 862 (1968).
123. Saegusa, T., Ito, Y., Kobayashi, S., Hiroto, K., and Takeda, N., *Can. J. Chem.* **47**, 1217 (1969).
124. Saegusa, T., Ito, Y., Kobayashi, S., Hirota, K., and Yoshioka, H., *Bull. Chem. Soc. Jap.* **42**, 3310 (1969).
125. Saegusa, T., Ito, Y., Tomita, S., and Kinoshita, H., *J. Org. Chem.* **35**, 670 (1970).
126. Saegusa, T., Ito, Y., Kinoshita, H., and Tomita, S., *Bull. Chem. Soc. Jap.* **43**, 877 (1970).
127. Saegusa, T., and Shimizu, T., *J. Org. Chem.* **35**, 3995 (1970).
128. Saegusa, T., Kobayashi, S., and Ito, Y., *J. Org. Chem.* **35**, 2118 (1970).
129. Saegusa, T., Murase, I., and Ito, Y., *J. Org. Chem.* **36**, 2876 (1971).
130. Saegusa, T., Ito, Y., Kinoshita, H., and Tomita, S., *J. Org. Chem.* **36**, 3316 (1971).
131. Saegusa, T., Ito, Y., Tanezawa, K., Inubushi, Y., and Tomita, S., *J. Amer. Chem. Soc.* **93**, 4049 (1971).

132. Saegusa, T., Ito, Y., and Tomita, S., *J. Amer. Chem. Soc.* **93**, 5656 (1971).
133. Sarapu, A., and Fenske, R. F., private communication.
134. Sarkar, S., Bandyopadhyay, P., and Sarkar, P. B., *J. Indian Chem. Soc.* **45**, 992 (1968).
135. Sato, M., Ishida, Y., and Nakamura, Y., *Nippon Kagaku Zasshi* **91**, 1188 (1970).
136. Schrauzer, G. N., and Lee, L. P., *J. Amer. Chem. Soc.* **90**, 6541 (1968).
137. Schrauzer, G. N., and Lee, L. P., *J. Amer. Chem. Soc.*, **92**, 1551 (1970).
138. Schrauzer, G. N., and Schlessinger, G., *J. Amer. Chem. Soc.* **92**, 1808 (1970); Schrauzer, G. N., Doemeny, P. A., Kiefer, G. W., and Frazier, R. H., *ibid.* **94**, 3604 (1972).
139. Stallick, J. K., and Ibers, J. A., *J. Amer. Chem. Soc.* **92**, 5333 (1970).
140. Stenson, J. P., Ph.D. Thesis, Univ. of Wisconsin (1970).
141. Stephany, R. W., and Drenth, W., *Recl. Trav. Chim. Pays-Bas* **89**, 305 (1970).
142. Strohmeier, W., and Mueller, F. J., *Chem. Ber.* **102**, 3613 (1969).
143. Treichel, P. M., and Stenson, J. P., *Inorg. Chem.* **8**, 2563 (1969).
144. Treichel, P. M., and Hess, R. W., *J. Amer. Chem. Soc.* **92**, 4731 (1970).
145. Treichel, P. M., and Hess, R. W., *J. Chem. Soc., D* 1626 (1970).
146. Treichel, P. M., Benedict, J. J., Hess, R. W., and Stenson, J. P., *J. Chem. Soc., D* 1627 (1970).
147. Treichel, P. M., Knebel, W. J., and Hess, R. W., *J. Amer. Chem. Soc.* **93**, 5424 (1971).
148. Treichel, P. M., Stenson, J. P., and Benedict, J. J., *Inorg. Chem.*, **10**, 1183 (1971); communication, Treichel, P. M., and Stenson, J. P., *J. Chem. Soc., D* 423 (1969).
149. Treichel, P. M., and Knebel, W. J., *Inorg. Chem.* **11**, 1285 (1972).
150. Treichel, P. M., and Knebel, W. J., *Inorg. Chem.* **11**, 1289 (1972).
151. Treichel, P. M., Wagner, K. P., and Knebel, W. J., *Inorg. Chim. Acta*, in press.
152. Treichel, P. M., and Smith, D. L., unpublished observations.
153. Treichel, P. M., and Wagner, K. P., unpublished observations.
154. Treichel, P. M., and Dirreen, G. E., *J. Organometal. Chem.* **39**, C20 (1972).
155. Treichel, P. M., and Knebel, W. J., *J. Coord. Chem.*, in press.
156. Ugi, I., ed., "Isonitrile Chemistry." Academic Press, New York, 1971.
157. Van Tamelen, E. E., Rudler, H., and Bjorklund, C., *J. Amer. Chem. Soc.* **93**, 3526 (1971).
158. Vaughn, L. G., and Shepherd, W. A., *J. Amer. Chem. Soc.* **91**, 6151 (1969).
159. von Ammon, R., Kanellakopulos, B., Fischer, R. D., and Lauberau, P., *Inorg. Nucl. Chem. Lett.* **5**, 315 (1969).
160. von Ammon, R., Fischer, R. D., and Kanellakopulos, B., *Chem. Ber.* **104**, 1072 (1971).
161. Walker, P. J. C., and Mawby, R. J., *J. Chem. Soc., A* 3006 (1971).
162. Wilford, J. B., Smith, N. O., and Powell, H. M., *J. Chem. Soc., A* 1544 (1968).
163. Yamamoto, Y., Yamazaki, H., and Hagihara, N., *Mem. Inst. Sci. Ind. Res., Osaka Univ.* **26**, 167 (1969).
164. Yamamoto, Y., Yamazaki, H., and Hagihara, N., *J. Organometal. Chem.*, **18**, 189 (1969); communication, *Bull. Chem. Soc. Jap.* **41**, 532 (1968).
165. Yamamoto, Y., and Hagihara, N., *Bull. Chem. Soc. Jap.* **42**, 2077 (1969).
166. Yamamoto, Y., and Yamazaki, H., *Bull. Chem. Soc. Jap.* **43**, 143 (1970).
167. Yamamoto, Y., and Yamazaki, H., *J. Organometal. Chem.* **24**, 717 (1970).
168. Yamamoto, Y., and Hagihara, N., *Mem. Inst. Sci. Ind. Res., Osaka Univ.* **27**, 109 (1970).
169. Yamamoto, Y., and Yamazaki, H., *Bull. Chem. Soc. Jap.* **43**, 3634 (1970).
170. Yamamoto, Y., and Yamazaki, H., *Bull. Chem. Soc. Jap.* **43**, 2653 (1970).
171. Yamamoto, Y., and Yamazaki, H., *Bull. Chem. Soc. Jap.* **44**, 1873 (1971).

172. Yamamoto, Y., and Yamazaki, H., *Inorg. Chem.* **11**, 211 (1972).
173. Japanese Patent 6,901,223 [*Chem. Abstr.*, **70**, 97417x (1969)].
174. Japanese Patent 7,028,574 [*Chem. Abstr.*, **74**, 3729h (1970)].
175. British Patent, 1,184,751 [*Chem. Abstr.*, **72**, 112035h (1970)].
176. British Patent 1,202,306 [*Chem. Abstr.*, **73**, 124947r (1970)].
177. U.S. Patent 3,560,409 [*Chem. Abstr.*, **75**, 26991x (1971)].

Insertion Reactions of Transition Metal–Carbon σ -Bonded Compounds I: Carbon Monoxide Insertion

ANDREW WOJCICKI

*Department of Chemistry
The Ohio State University
Columbus, Ohio*

List of Abbreviations	88
I. Introduction to and Scope of Insertion Reactions	88
II. Carbon Monoxide Insertion. General Considerations and Background	90
III. Kinetics and Mechanism of Carbon Monoxide Insertion	94
A. Perspective	94
B. Role of Solvent	97
C. Effect of Entering Ligand	99
D. Effect of Alkyl Group	101
E. Effect of Ancillary Ligands	102
F. Intratriad Trends	103
G. Comparison of Various Systems	103
IV. Kinetics and Mechanism of Decarbonylation	105
A. Scope	105
B. Thermal Decarbonylation	105
C. Photolytic Decarbonylation	111
D. Chemical Decarbonylation	111
V. Stereochemistry of Carbonylation and Decarbonylation	112
VI. Survey of Reactions	117
A. Titanium and Vanadium Triads	118
B. Chromium Triad	118
C. Manganese Triad	122
D. Iron Triad	126
E. Cobalt Triad	131
F. Nickel Triad	137
G. Copper Triad	139
References	139

List of Abbreviations

In order to conserve space, the following abbreviations, listed alphabetically, will be used in the text and in the tables:

Bu	Butyl
Cp	π (or h^3)-Cyclopentadienyl
Cpr	Cyclopropyl
Et	Ethyl
L, L'	Monodentate ligand (usually nonionic)
Me	Methyl
Ph	Phenyl
Pr	Propyl
R, R'	Hydrocarbon radical or diradical (may include R _F)
R _F	Perfluorocarbon radical or diradical
Tdp	Tris(dimethylamino)phosphine
THF	Tetrahydrofuran

I

INTRODUCTION TO AND SCOPE OF INSERTION REACTIONS

Numerous organometallic reactions conform to the general equation

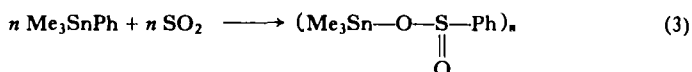
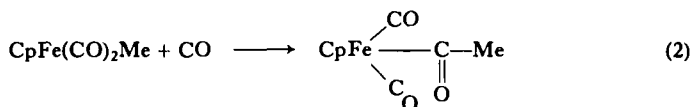


where M is a metal and X and Y are monatomic or polyatomic species (ancillary ligands have been omitted). Such processes are termed "insertion reactions." The name has been used in a broad context and carries no mechanistic connotations. It merely reflects the overall structural change resulting from interposition of an unsaturated species, Y, into a metal-element (M—X) bond.

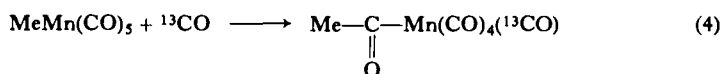
Of various possible classifications of insertion reactions three are considered here.

(1) The insertions may be grouped according to the nature of M—X and Y. M—X linkages which are known to engage in such processes include metal-hydrogen, metal-carbon, metal-halogen, metal-oxygen, and metal-metal, to mention a few. Some of the more common inserting molecules are CO, SO₂, SO₃, carbenes, olefins, and organic isocyanides.

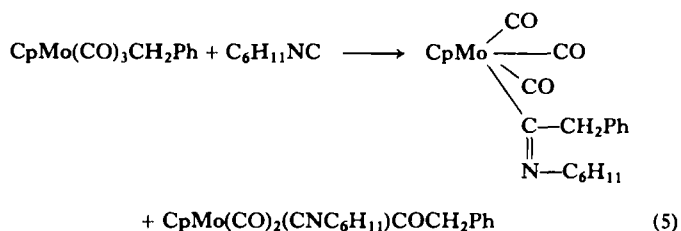
(2) Alternatively, the insertions may be regarded as additions of M and X to the unsaturated substrate Y. In this context, 1,1 [Eq. (2)] (70), 1,2 [Eq. (3)] (91), etc., additions have been recognized.



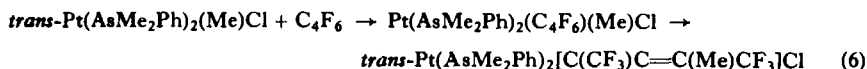
(3) Thirdly, insertion reactions may sometimes be considered as being inter- or intramolecular depending on whether Y was precoordinated to M. Thus Eq. (4) furnishes one example of an intramolecular insertion (191).



However, the formation of $\text{CpMo(CO)}_3\text{C(CH}_2\text{Ph)=NC}_6\text{H}_{11}$ in Eq. (5)

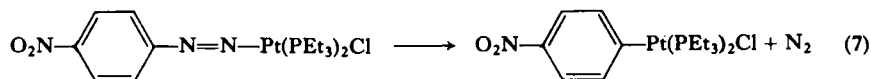


almost certainly proceeds via an intermolecular insertion (246). The obvious limitation of this classification is our inability always to ascertain whether an intermediate of the type M(X)Y [Eq. (1)] has been formed. Several coordinatively unsaturated transition metal complexes, for example, square-planar Pt(II) , have been shown to increase their coordination number to 5 before undergoing insertion [Eq. (6)] (67). Hence, these and related compounds may be regarded as inserting intramolecularly.



Some insertion reactions, particularly those of carbon monoxide, are reversible, but many are not. Reactions have also been reported which result in extrusion of Y from M—Y—X , even though the reverse of this process [Eq. (1)] is not known to occur. Elimination of N_2 from arylazo

platinum complexes to give the corresponding arylplatinum compounds is an example of such behavior [Eq. (7)] (202).



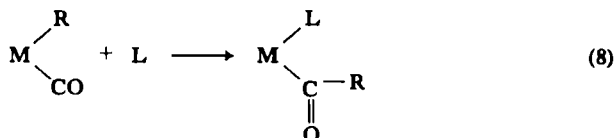
Much of the recent interest in insertion reactions undeniably stems from the emphasis placed on development of homogeneous catalysis as a rational discipline. One or more insertion is involved in such catalytic processes as the hydroformylation (31) or the polymerization of olefins (26, 75) and isocyanides (244). In addition, many insertion reactions have been successfully employed in organic and organometallic synthesis. The research in this general area has helped systematize a large body of previously unrelated facts and opened new areas of chemistry for investigation. Heck (114) and Lappert and Prokai (161) provide a comprehensive compilation and a systematic discussion of a wide variety of insertion reactions in two relatively recent (1965 and 1967) reviews.

This chapter is concerned entirely with the insertion of carbon monoxide into transition metal-carbon σ -bonds. Sulfur dioxide insertion (154, 239), also common among transition metal-carbon complexes, will be treated in a complementary review, which is to appear later. Subject to the restrictions given at the beginning of Section VI, an attempt has been made at a complete literature coverage of the insertion of CO. Particular emphasis focuses on recent results, especially those of a kinetic and stereochemical nature.

II

CARBON MONOXIDE INSERTION. GENERAL CONSIDERATIONS AND BACKGROUND

Carbon monoxide insertion reactions may be represented by the equation:

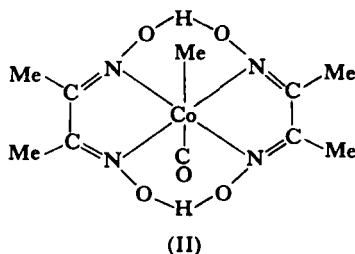
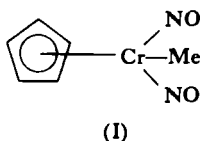


where $\text{M}(\text{CO})\text{R}$ is a reactant or an intermediate, R is an alkyl or a related

σ -bonded carbon group,¹ L stands for any ligand, including CO, and M represents a metal together with its ancillary ligands. In all cases a 1,1-addition (acyl) rather than a 1,2-addition (carbene-like, $M-C-O-R$) product is obtained. Structures of several acyl metal complexes, including $CpMo(CO)_2(PPh_3)COMe$ (65) and $p-ClC_6H_4CRe(CO)_5$ (6), have been determined by X-ray crystallography. Where such direct evidence is not available, the infrared and/or proton NMR spectra usually serve as reliable guides in ascertaining the nature of these products.

Some transition metal systems $M(CO)R$ react with a wide range of L, including phosphites, phosphines, arsines, stibines, organic amines, iodide, and CO, to mention a few, yielding the corresponding acyls. Other systems, e.g., $CpFe(CO)_2R$ (28), display a marked selectivity toward various L. Certain unsaturated molecules L [SO_2 (239), $CF_2=CF_2$ (238), *inter alia*] insert themselves into the $M-R$ bond instead of effecting the reaction shown in Eq. (8).

Carbon monoxide insertions are intramolecular. It therefore follows that an important requirement for occurrence of these processes is presence of the CO and R in the reacting complex in a suitable position to combine. Accordingly, compound (I) does not react with CO under ambient conditions (105). The dinuclear $[MeCo(DH)_2]_2$ (DH = dimethylglyoximate) reacts with CO, but not by insertion, to give (II) in solution (125). Forma-



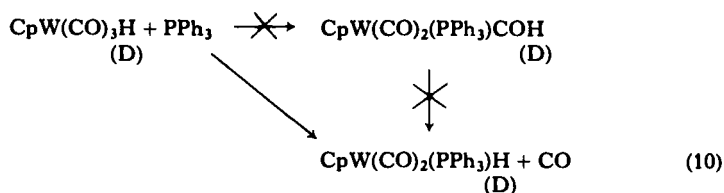
tion of an acyl on further exposure of (II) to CO is apparently prevented by an unfavorable disposition of R and the coordinated CO. Coordinatively unsaturated square-planar $Pt(II)$ and $Pd(II)$ complexes $RM(PR'_3)_2X$ do not satisfy the foregoing requirement but nevertheless undergo CO insertion



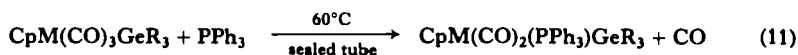
¹ Henceforth the words *alkyl* and *acyl*, unless qualified, have a broad meaning and include phenyl, perfluoroalkyl, etc., moieties.

[Eq. (9): $M = \text{Pt}$ and Pd , $R = \text{Me}$, Et , and Ph , $R' = \text{Et}$] (39). However, in these cases, a five-coordinate carbonyl, $\text{RM}(\text{CO})(\text{PR}'_3)_2\text{X}$ is a likely precursor of the acyl.

Carbon monoxide insertion is not restricted to transition metal-carbon bonds, although $\text{M}-\text{C}$ is by far the most common substrate involved. Reactions have also been reported which lead to insertion of CO into $\text{M}-\text{O}$ (114) and $\text{M}-\text{N}$ (199) bonds. 1,1-Additions of $\text{M}-\text{H}$ (27, 114) and $\text{M}-\text{M}$ (104) linkages to CO have been postulated, too. However, direct replacement of CO , without rupture of the $\text{W}-\text{H}$ bond, is indicated for the reaction between $\text{CpW}(\text{CO})_3\text{H}$ (or $-\text{D}$) and PPh_3 (8):

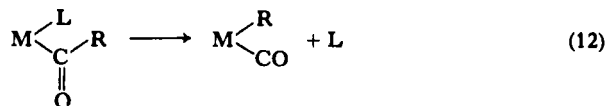


Another interesting substitution [Eq. (11): $M = \text{Mo}$ and W , $R = \text{Me}$, Et or $i\text{-Pr}$] (57) proceeds via the intermediacy of a pale brown material which

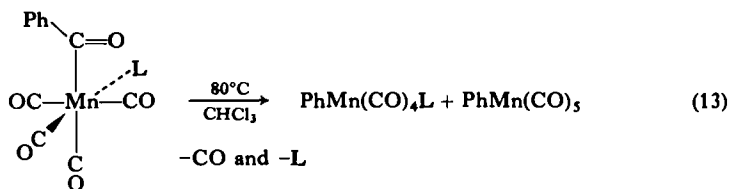


analyzes for $\text{CpM}(\text{CO})_3(\text{PPh}_3)\text{GeR}_3$. However, the infrared spectrum of this species shows no $\nu(\text{CO})$ of MCOGeR_3 , apparently ruling out CO insertion into the $\text{M}-\text{Ge}$ bond.

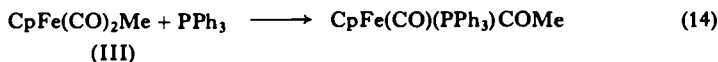
One of the properties of transition metal acyl complexes is their ability to lose CO , usually on heating or photolysis. This so-called decarbonylation often represents a special case of the reverse of the CO insertion in Eq. (8), where $L = \text{CO}$.



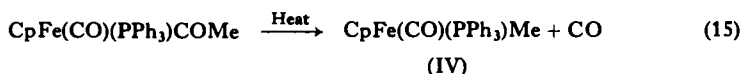
However, L other than CO can be lost instead of or in competition with carbon monoxide [Eq. (13): $L = \text{P}(\text{OCH}_2)_3\text{CEt}$] (35).



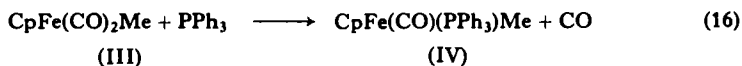
Whereas some acyl products, especially RCOMn(CO)_5 and RCOCu(CO)_4 , easily eliminate carbon monoxide via the reverse of the insertion, others decarbonylate through a different route. For example, the reaction



(28) is not reversible, the elimination of CO from the acyl proceeding as per Eq. (15) (219). Accordingly, when reaction of (III) with PPh_3 is conducted

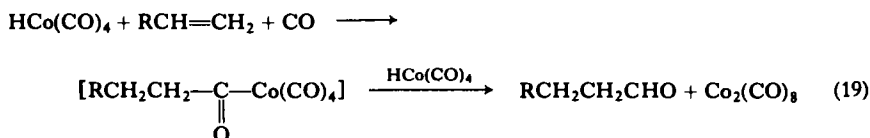
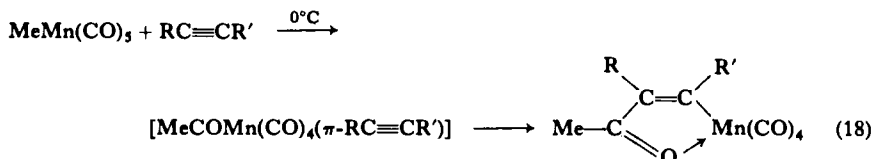
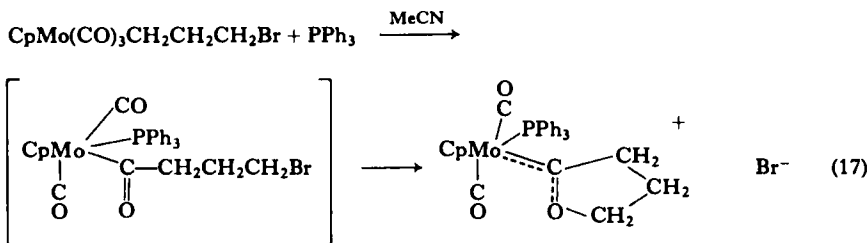


under vigorous conditions and over an extended period, only (IV) may be detected (219). This may lead to an erroneous conclusion that the formation of (IV) proceeds via a direct replacement of CO in (III) with PPh_3 [Eq. (16)]



rather than in two discrete steps. Since reactions between transition metal alkyls and Lewis bases are frequently carried out under preparative, and therefore generally vigorous conditions, a cautious mechanistic interpretation of the literature data may be required. It is relevant, however, that the photochemical reaction between (III) and PPh_3 takes place directly (219, 227), as shown in Eq. (16).

Additional complications with regard to recognition of an insertion reaction may arise if the acyl produced defies isolation by undergoing a further transformation. Equations (17)–(19) (78, 134, 115) provide diversified examples of such behavior (the postulated CO insertion intermediates are enclosed in brackets). The intermediacy of acyl complexes in these reactions can sometimes be inferred through examination of the infrared or NMR spectra of reaction solutions. In a number of cases, however,



evidence is less direct or even nonexistent. Mechanistic inferences in such situations are made by consideration of various possible pathways and by analogy with reactions of related systems.

This chapter is concerned initially with kinetic results and mechanistic interpretations of the CO insertion (Section III) and extrusion (Section IV) reactions. A discussion of the stereochemical data follows (Section V), and a comprehensive survey of these reactions by the triads (Section VI) rounds out the review. Carbon monoxide insertion reactions were discussed in 1967 by Basolo and Pearson (21). Since then they have been mentioned in several reviews (49, 118, 203, *inter alios*) but have not been treated comprehensively.

III

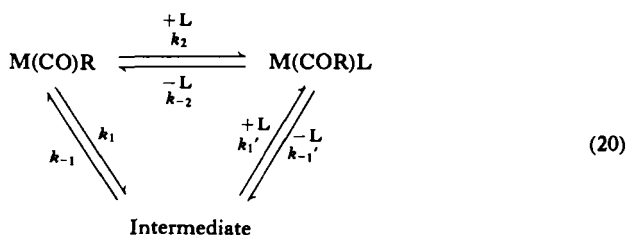
KINETICS AND MECHANISM OF CARBON MONOXIDE INSERTION

A. Perspective

Kinetic studies have been conducted on reactions of RMn(CO)_5 (37, 50–52, 54, 97, 168), $\text{CpFe(CO)}_2\text{R}$ (48, 98), $\pi\text{-C}_x\text{H}_y\text{Mo(CO)}_3\text{R}$ (48, 79–81,

108), $\text{RPt}(\text{CO})\text{LX}$ (93), and $\text{RIr}(\text{CO})_2\text{LX}_2$ (92) $[\text{M}(\text{CO})\text{R}]$ with various nucleophiles (L') to give the corresponding $\text{M}(\text{COR})\text{L}'$. In addition, kinetic data have been reported for reactions of $\text{Rh}(\text{CO})_2\text{LX}^2$ (233) and $\text{Rh}(\text{CO})\text{L}_2\text{X}$ (88) $[\text{M}(\text{CO})]$ with RX' which proceed in two steps—oxidative addition and CO insertion—to afford $\text{M}(\text{COR})\text{X}'$.

The results can be accommodated by the following general mechanism:



By applying the steady-state approximation for the concentration of the intermediate one obtains:

$$\frac{d[\text{M}(\text{COR})\text{L}]}{dt} = k_1[\text{M}(\text{CO})\text{R}] - k_{-1} \left[\frac{k_1[\text{M}(\text{CO})\text{R}] + k_{-1}'[\text{M}(\text{COR})\text{L}]}{k_{-1} + k_1'[\text{L}]} \right] + k_2[\text{M}(\text{CO})\text{R}][\text{L}] - k_{-2}[\text{M}(\text{COR})\text{L}] \quad (21)$$

Since most insertion reactions go to virtual completion, k_{-1}' and k_{-2} may be ignored, simplifying Eq. (21) to

$$\frac{d[\text{M}(\text{COR})\text{L}]}{dt} = \frac{k_1 k_1'[\text{M}(\text{CO})\text{R}][\text{L}]}{k_{-1} + k_1'[\text{L}]} + k_2[\text{M}(\text{CO})\text{R}][\text{L}] \quad (22)$$

The two terms in Eq. (22) pertain to what shall be called the k_1 path and the k_2 path, respectively. Further simplification of the rate equation is possible by one or more of the following considerations:

(a) Only the k_1 path is operative; i.e., there is no direct interaction of the alkyl with L. In this case:

(i) If k_{-1} is very small compared to $k_1'[\text{L}]$, i.e., if the reactive intermediate is more effectively captured by L than it reverts to the alkyl, the rate expression becomes

$$\frac{d[\text{M}(\text{COR})\text{L}]}{dt} = k_1[\text{M}(\text{CO})\text{R}] \quad (23)$$

and first-order kinetics are observed.

² This compound has recently been reformulated. See refs. (174), (204), and (216).

(ii) If k_{-1} is appreciable and $k'_1[L]$ is small, one obtains

$$\frac{d[M(\text{COR})L]}{dt} = \frac{k_1 k'_1}{k_{-1}} [M(\text{CO})R][L] \quad (24)$$

reflecting second-order kinetics, first-order in both $[M(\text{CO})R]$ and $[L]$. This often occurs when the concentration of L is low as, for example, when $L = \text{CO}$. In theory, but not always readily in practice, this situation can be ascertained by increasing the concentration of L .

(iii) If k_{-1} is comparable to $k'_1[L]$, then k_{obs} , given by the expression

$$k_{\text{obs}} = \frac{k_1 k'_1 [L]}{k_{-1} + k'_1 [L]} \quad (25)$$

increases with $[L]$, approaching a limiting value at high concentrations. A plot of $1/k_{\text{obs}}$ vs. $1/[L]$ is linear, the slope being $k_{-1}/k_1 k'_1$, and the intercept $1/k_1$ Eq. (26). An invariance of k_1 to changes in the ligand L lends further support to this scheme.

$$\frac{1}{k_{\text{obs}}} = \frac{k_{-1}}{k_1 k'_1} \left(\frac{1}{[L]} \right) + \frac{1}{k_1} \quad (26)$$

(b) The k_2 path is being followed either alone or in conjunction with the k_1 path. Provided that $[L]$ is sufficiently high (a condition which can be satisfied with most ligands), minimizing the relative importance of k_{-1} , Eq. (22) becomes

$$\frac{d[M(\text{COR})L]}{dt} = k_1 [M(\text{CO})R] + k_2 [M(\text{CO})R][L] \quad (27)$$

or

$$\frac{d[M(\text{COR})L]}{dt} = k_{\text{obs}} [M(\text{CO})R] \quad (28)$$

where

$$k_{\text{obs}} = k_1 + k_2 [L] \quad (29)$$

By plotting k_{obs} vs. $[L]$ one obtains a straight line whose slope is k_2 and the intercept k_1 .

All of these limiting situations have been encountered in practice, as will be seen in the ensuing discussion.

B. Role of Solvent

1. Effect on the Reactivity and Mechanism

Transition metal alkyls may be divided into two categories with respect to solvent dependence of their CO insertions:

- (i) Those whose reactions depend on the nature of the solvent.
- (ii) Those which react by the k_1 path and are not influenced by the solvent employed.

Group (ii) includes $\text{RIr}(\text{CO})_2\text{LCl}_2$ and $\text{RPt}(\text{CO})\text{LCl}$ ($\text{L} = \text{AsR}_3$). Some representative data for the reaction of $\text{EtPt}(\text{CO})(\text{AsPh}_3)\text{Cl}$ with AsPh_3 are given in Table I.

Belonging to group (i) are alkylmetal carbonyls and cyclopentadienylmetal alkyl carbonyls of formula $\text{RMn}(\text{CO})_5$, $\text{CpFe}(\text{CO})_2\text{R}$, and $\text{CpMo}(\text{CO})_3\text{R}$. Solvent dependence of the reaction of $\text{MeMn}(\text{CO})_5$ with $\text{C}_6\text{H}_{11}\text{NH}_2$ is illustrated also in Table I. The rate varies markedly with the dielectric constant and with the nucleophilic power of the solvent. For example, on going from dimethylformamide to mesitylene, the rate of insertion is reduced by $\sim 10^4$. Similarly, the sequence $\text{MeCN} \gg \text{Me}_2\text{CO} > \text{THF} > \text{CHCl}_3 > \text{C}_6\text{H}_6$ was reported for the reaction of $\text{MeMn}(\text{CO})_5$ with $\text{P}(\text{OCH}_2)_3\text{CR}$ ($\text{R} = \text{Me}$ and Et) in various solvents (97). Analogous trends were observed for the insertion reactions of $\text{CpFe}(\text{CO})_2\text{R}$ and $\text{CpMo}(\text{CO})_3\text{R}$ (48, 80, 98).

In addition to influencing the reactivity, the coordinating ability of the solvent affects the mechanism of CO insertion. Thus, when a poorly coordinating solvent is employed together with a good nucleophile L, the k_1 path is almost invariably suppressed and the k_2 path takes over (Table I, reaction 6). Moreover, when the solvent effectively competes with L for the reactive intermediate ($k'_1[\text{L}]$ comparable to k_{-1}), a dependence of the rate on $[\text{L}]$ toward a limiting value is observed (Table I, reaction 2).

2. Nature of the Reactive Intermediate

Evidence for the reactive intermediate in Eq. (20) is strictly of a kinetic nature. Since attempts at its detection by proton NMR spectroscopy starting with $\text{RMn}(\text{CO})_5$ or $\text{CpMo}(\text{CO})_3\text{R}$ were not successful (80, 81, 97), such a species must be present in low concentrations.

For the reactions proceeding without an appreciable involvement of the

TABLE I
INFLUENCE OF SOLVENT ON RATES OF CO INSERTION

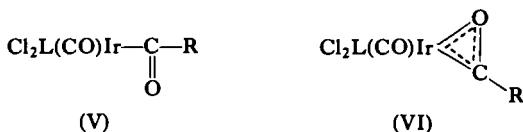
Reaction No.	Solvent	Dep. on conc. of reactants ^a	k_1 (sec ⁻¹)	k_2 (M ⁻¹ sec ⁻¹)	Dielectric const.
(a) $\text{MeMn(CO)}_5 + \text{C}_6\text{H}_{11}\text{NH}_2 \rightarrow \text{MeCOMn(CO)}_4(\text{C}_6\text{H}_{11}\text{NH}_2)$ ^b					
1	Dimethylformamide	Reaction too fast to determine	$> 1.5 \times 10^{-2}$	—	26.6
2	Methanol	a (iii)	6.33×10^{-3}	—	31.2
3	Nitromethane	a (i)	1.66×10^{-3}	—	37.4
4	THF	a (i)	9.63×10^{-4}	—	7.70
5	Mesitylene	b	2.18×10^{-6}	1.11×10^{-4}	2.27
6	Hexane	b	Too small, if any	2.70×10^{-5}	1.91
(b) $\text{EtPt(CO)(AsPh}_3\text{)Cl} + \text{AsPh}_3 \rightarrow \text{EtCOPt(AsPh}_3\text{)}_2\text{Cl}$ ^c					
7	1,2-Dichloroethane	a (i)	14.0×10^{-4}	—	10.4
8	Nitrobenzene	a (i)	11.4×10^{-4}	—	34.8
9	Chlorobenzene	a (iii), assumed	7.57×10^{-4}	—	5.6
10	THF	a (iii)	4.92×10^{-4}	—	7.70

^a See Section III,A for notations.

^b At 25.5°C; from Mawby *et al.* (168).

^c At 40.0°C; from Glyde and Mawby (93).

solvent (group (i), Section 1), this intermediate may be either a coordinatively unsaturated acyl complex or a π -acyl derivative. In the case of $\text{RIr}(\text{CO})_2\text{LCl}_2$ this would correspond to structures (V) and (VI), respectively. What appear to be the first examples of a π -bonded acyl complex, $\text{RCORu}(\text{CO})(\text{PPh}_3)_2\text{Cl}$ ($\text{R} = \text{Me}$ and Et), have recently been reported (132).



That the intermediate is an acyl rather than, for example, an alkyl receives support from kinetic and stereochemical studies on reactions of $\text{MeCO-Mn}(\text{CO})_5$ (Sections IV, V).

When solvent does play a major role in the k_1 path [group (ii) reactions]—a mechanism referred to as the solvent-assisted pathway—the structure of the intermediate is even less certain. Basolo and co-workers (168) favor a solvated acyl complex such as, for example, $\text{RCOMn}(\text{CO})_4\text{S}$ ($\text{S} = \text{solvent}$). This is principally on the grounds that the coordinating ability of the solvent, and not only its dielectric constant, appear to influence the rate of insertion (see Table I, reactions 2 and 3: $\text{MeOH} > \text{MeNO}_2$). Additional support derives from the large negative entropy of activation for these reactions (Section III, G). It has been suggested that the breaking of the $\text{M}-\text{R}$ bond is assisted by the solvent. Formation of the acyl moiety is then complete with the entry of a solvent molecule into the coordination sphere of the metal. By way of contrast, Craig and Green (80, 81) prefer an unsolvated structure for the intermediate. Their preference is influenced by stereochemical considerations (Section V).

C. Effect of Entering Ligand

This is intimately related to the nature of the solvent. If the solvent is nonpolar and lacks coordinating ability, then generally [known exceptions are the $\text{Pt}(\text{II})$ and $\text{Ir}(\text{III})$ complexes mentioned in Section B] the insertion will proceed via attack of L upon the alkyl compound (k_2 path), e.g., Table I, reaction 6.

However, in a solvent that is polar and or capable of coordination, competition will exist between the reaction of the intermediate with L to give

the acyl product and its reversion to the alkyl. If L is a sufficiently good nucleophile to capture the intermediate (whether solvated or not), then the k_1 path prevails either alone (e.g., Table II, reactions 1–5) or in parallel with the k_2 path (e.g., Table II, reactions 6 and 7). If not, then the insertion may still proceed via the k_2 path, e.g., Table II, reactions 8 and 9.

TABLE II
REPRESENTATIVE CO INSERTIONS WITH DIFFERENT L

Reaction No.	L	k_1 (sec^{-1})	k_{-1}/k'_1 (M)	k_2 ($\text{M}^{-1} \text{sec}^{-1}$)
(a) $\text{CpFe}(\text{CO})_2\text{Et} + \text{L} \xrightarrow{\text{MeCN}} \text{CpFe}(\text{CO})\text{L}(\text{COEt})^a$				
1	PPh_3	1.32×10^{-4}	0.36	—
2	PMe_2Ph	2.22×10^{-4}	0.41	—
3	PMePh_2	1.78×10^{-4}	0.35	—
4	$\text{P}(\text{OMe})_3$	1.84×10^{-4}	0.54	—
5	$\text{P}(\text{OPh})_3$	1.35×10^{-4}	0.81	—
(b) $\text{CpMo}(\text{CO})_3\text{Me} + \text{L} \xrightarrow{\text{toluene}} \text{CpMo}(\text{CO})_2\text{L}(\text{COMe})^b$				
6	$\text{P}(n\text{-Bu})_3$	5.80×10^{-6}	—	6.44×10^{-5}
7	$\text{P}(n\text{-OBu})_3$	5.80×10^{-6}	—	5.00×10^{-5}
8	PPh_3	—	—	3.22×10^{-5}
9	$\text{P}(\text{OPh})_3$	—	—	8.33×10^{-6}

^a At 47.5°C; from Green and Westlake (98).

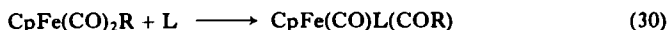
^b At 50.7°C; from Butler *et al.* (48).

Few quantitative data are available on the relative nucleophilicities of L toward various alkyl carbonyls. The rates of the reaction of $\text{CpMo}(\text{CO})_3\text{Me}$ with L in toluene (Table II) decrease as a function of the latter reactant: $\text{P}(n\text{-Bu})_3 > \text{P}(n\text{-OBu})_3 > \text{PPh}_3 > \text{P}(\text{OPh})_3$, but the spread is relatively small (<8). The above order is that customarily observed for $\text{S}_{\text{N}}2$ reactions of low-valent transition metal complexes (3, 214). Interestingly, neither $\text{CpMo}(\text{CO})_3\text{Me}$ nor $\text{CpFe}(\text{CO})_2\text{Me}$ reacts with I^- or N, S, and As donor ligands (28, 79). This is in direct contrast to the insertion reactions of $\text{MeMn}(\text{CO})_5$ which manifest much less selectivity toward various L (see Section VI,B,C,D for details).

D. Effect of Alkyl Group

Rather limited information is available on how the nature of R affects the rate of CO insertion, all other factors being constant. A generalization that ethylmetal complexes react faster than the corresponding methyl carbonyls derives from investigations on four systems: $\text{RIr}(\text{CO})_2(\text{AsPh}_3)\text{Cl}_2$ (92), $\text{RMn}(\text{CO})_5$ (51), $\text{CpFe}(\text{CO})_2\text{R}$ (98), and $\text{CpMo}(\text{CO})_3\text{R}$ (80). When $\text{R} = \text{Et}$ the reactions with CO or P and As donor ligands proceed at least ~6 times faster than when $\text{R} = \text{Me}$.

In another study pertinent to the theme, Green and Westlake (98) examined the kinetics of the reaction



where L is a phosphine or a phosphite. In acetonitrile these insertions proceed via a solvent-assisted k_1 path, and the reactivity decreases: $\text{R} = i\text{-Pr} > \text{Et} > \text{Me}$. The values of ΔH^\ddagger increase in this same order, reflecting the importance of the effect Fe—C (R) bond strength on the relative rates of insertion. An investigation of a related reaction (80, 81)

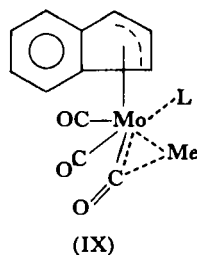
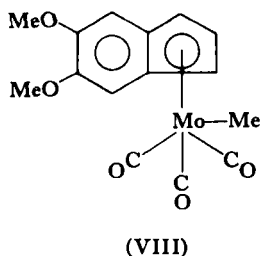
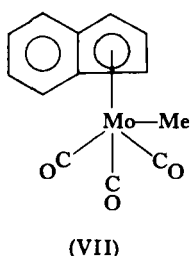


also in MeCN, showed that at 30.5–40°C the rates decrease with R as $\text{Et} > \text{Me} (\sim 15) > \text{CH}_2\text{Ph} (7\text{--}8) > \text{CH}_2\text{CH}=\text{CH}_2 (1)$. The authors took this to suggest that little or no charge separation occurs in the step $\text{Mo}(\text{CO})\text{R} \rightarrow \text{Mo}(\text{COR})$.

The rates of the carbonylation of $\text{RMn}(\text{CO})_5$ with CO in 2,2'-diethoxy-diethyl ether at 30°C were reported by Calderazzo and Cotton (51). They decrease in the order: $\text{R} = n\text{-Pr} (16) > \text{Et} (13) > \text{Ph} (1.7) > \text{Me} (1) \gg \text{CH}_2\text{Ph}$ and CF_3 , the last two alkyls reacting immeasurably slowly. It is of interest that $\text{PhCH}_2\text{Co}(\text{CO})_4$ also carbonylates slowly compared to other $\text{RCo}(\text{CO})_4$ alkyls (177). Thus, electron-releasing R groups enhance the rate, whereas electron-withdrawing R groups slow it down. Replacement of H in R with F invariably reduces the rate of CO insertion by strengthening the M—R linkage. The reactivity order: $\text{MeMn}(\text{CO})_5 > \text{FCH}_2\text{Mn}(\text{CO})_5 \gg \text{CF}_3\text{Mn}(\text{CO})_5$ toward ligands effecting the insertion offers an example of this behavior (54). It is significant that incorporation of CO into a transition metal-perfluoroalkyl or -perfluoroaryl bond has yet to be reported. Similar general trends have been noted for substitution and other insertion reactions (3, 239).

E. Effect of Ancillary Ligands

Again, this aspect of carbon monoxide insertion has not received much attention. Hart-Davis and Mawby (108), in a comparative study, examined the reaction of $\pi\text{-C}_9\text{H}_7\text{Mo(CO)}_3\text{Me}$ (VII) with various P donor ligands. They find that, in THF, (VII) undergoes CO insertion, via a solvent-assisted



path, ~ 20 times faster than the corresponding $\text{CpMo(CO)}_3\text{Me}$. In hexane it reacts with $\text{P}(n\text{-Bu})_3$ about 10 times faster than does $\text{CpMo(CO)}_3\text{Me}$, by an $\text{S}_{\text{N}}2$ path. A substituted π -indenyl complex, (VIII), reacts in THF more slowly than does (VII), but only by a factor of 2. This suggests that the enhancement of the rate on going from $\text{CpMo(CO)}_3\text{Me}$ to (VII) is not due principally to replacement of Cp with the better electron-withdrawing $\pi\text{-C}_9\text{H}_7$. The authors propose that a π -allyl type of structure for (VII) may be important and contributes by making a vacant molybdenum orbital available for attack by L [see (IX)]. Similarities in the values of $\nu(\text{CO})$ for $\text{CpMo(CO)}_3\text{Me}$ and (VII) indicate that the stabilities of the respective ground states are essentially the same.

For the reaction of $\text{EtIr(CO)}_2\text{LCl}_2$ with L to give $\text{EtCOIr(CO)L}_2\text{Cl}_2$, the rates decrease with L: P donor \gg $\text{AsMe}_2\text{Ph} > \text{AsPh}_3$ (92). Since the entering L does not affect the reactivity, it appears that a higher basicity of ligand L already in the complex promotes the union of Et and CO to give COEt . However, the opposite trend is observed for the alkyl-to-acyl rearrangement of $\text{MeRh(CO)L}_2\text{ClI}$ in MeI (88). The rates at 25°C vary with L in the order: $p\text{-C}_6\text{H}_4\text{F} > p\text{-C}_6\text{H}_4\text{OMe}$. The values of ΔH^\ddagger (11.2 kcal/mole, $p\text{-C}_6\text{H}_4\text{F}$; 22.3 kcal/mole, $p\text{-C}_6\text{H}_4\text{OMe}$) reflect a weakening of the Rh—Me bond as the phosphine becomes less basic.

Recently, an abstract has been published (83) of a kinetic study of reactions of $\text{RMn(CO)}_3\text{L}_2$ (L = P donor ligand) with CO. No data were disclosed, however.

F. Intratriad Trends

No comparative kinetic study has been made on the same alkyl carbonyl system for two members of a given transition metal triad. Qualitative data show that the middle member is more reactive than the heaviest one; e.g., $\text{CpMo}(\text{CO})_3\text{R} \gg \text{CpW}(\text{CO})_3\text{R}$ (Section VI,B), $\text{Rh(III)} > \text{Ir(III)}$ (Section VI,E), and $\text{Pd(II)} > \text{Pt(II)}$ (Section VI,F). However, the extreme unreactivity of $\text{CpW}(\text{CO})_3\text{R}$ and a considerable difference in lability between most alkyls of Rh(III) and Ir(III) , as well as those of Pd(II) and Pt(II) , have prevented detailed investigations. Surprisingly, no kinetic studies have been conducted on insertion reactions of $\text{RRe}(\text{CO})_5$, which would seem readily amenable to such investigations.

G. Comparison of Various Systems

The objective of this section is to compare relative reactivities, as well as the activation parameters, for the CO insertion of various types of metal alkyl. Reference will be made again to the classification of these complexes introduced in Section B,1. Some of the data examined are contained in Table III.

Within group (i), square-planar $\text{EtPt}(\text{CO})(\text{AsPh}_3)\text{Cl}$ inserts more rapidly than six-coordinate $\text{EtIr}(\text{CO})_2(\text{AsPh}_3)\text{Cl}_2$. In THF at 40°C , the relative k 's are ~ 9 and 1 . Comparison of group (ii) alkyl carbonyls reveals the order: $\text{MeMn}(\text{CO})_5 > \text{CpMo}(\text{CO})_3\text{Me} > \text{CpFe}(\text{CO})_2\text{Me}$. The ratios of the k 's are $\sim 23:1$ and $100:1$, respectively, in THF at 25° and 50.7°C . The higher reactivity of manganese than of molybdenum is a consequence of the relative entropies, whereas the lowest reactivity of iron is caused by its ΔH^\ddagger (Table III).

It is interesting to note that, in general, CO insertion reactions of group (ii) alkyls have much more negative ΔS^\ddagger values and lower ΔH^\ddagger values than those of group (i) alkyls. Typically, ΔS^\ddagger will fall in the range -33 to -17 and -8 to 2 e.u., and ΔH^\ddagger will be 12 to 18 and 19 to 25 kcal/mole for group (ii) and (i) complexes, respectively. However, exceptions have been noted for group (ii). For example, the reactions of $\text{CpFe}(\text{CO})_2\text{Me}$ with $\text{P}(n\text{-Bu})_3$ in THF (Table III) and of $\text{PhMn}(\text{CO})_5$ with $\text{P}(\text{OCH}_2)_3\text{CEt}$ in MeNO_2 (37) proceed by the k_1 path with $\Delta S^\ddagger = -4$ and 0 e.u. and $\Delta H^\ddagger = 26$ and 22 kcal/mole, respectively. The more negative ΔS^\ddagger values generally observed for group (ii) alkyls no doubt result from involvement of the solvent (or L, for the k_2 path) in the transition state.

TABLE III
REPRESENTATIVE DATA FOR CO INSERTION OF VARIOUS TYPES OF METAL ALKYL

M	R	L	M(CO)R + L $\xrightarrow{\text{THF}}$ M(COR)L					Reference
			Temp. (°C)	Dep. on conc. of reactants ^a	k_1 (sec ⁻¹)	ΔS^\ddagger (e.u.)	ΔH^\ddagger (kcal/mole)	
Pt(AsPh ₃)Cl	Et	AsPh ₃	40.0	a (iii)	49.2×10^{-5}	-6.0	21.4	(93)
Ir(CO)(AsPh ₃)Cl ₂	Et	AsPh ₃	40.0	a (i)	5.8×10^{-5}	1.8	25.0	(92)
Mn(CO) ₄	Me	C ₆ H ₁₁ NH ₂	25.5	a (i)	9.63×10^{-4}	-17	16.6	(168)
CpFe(CO)	Me	P(<i>n</i> -Bu) ₃	50.7	a (iii)	3.86×10^{-6}	-4	26.1	(48)
CpMo(CO) ₂	Me	P(<i>n</i> -OBu) ₃	50.7	a (i)	3.94×10^{-4}	-25	16.1	(48)

^a See Section III,A for notations.

IV

KINETICS AND MECHANISM OF DECARBONYLATION

A. Scope

Elimination of carbon monoxide accompanied by conversion of an acyl group to the corresponding alkyl moiety has been termed decarbonylation. The process is represented by Eq. (12) with $L = CO$.

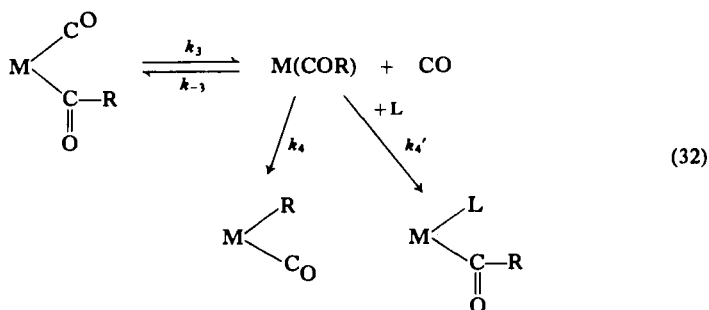
The decarbonylation can be effected (1) thermally, (2) photolytically, and (3) chemically, by using a metal complex such as $Rh(PPh_3)_3Cl$. The three types of processes will be considered in turn.

B. Thermal Decarbonylation

1. Perspective

This is the most extensively, as well as intensively, studied type of the decarbonylation. Nevertheless, kinetic data are scarce. Conversion of metal acyls to their respective alkyls has been investigated for two systems: $RCOMn(CO)_5$ (37, 50, 51) and $XCH_2COIr(PPh_3)_2Cl_2$ ($X = Ph$ or a substituted Ph group) (160).

Given in Eq. (32) is a general mechanistic scheme for the decarbonylation; ligand substitution is included for comparison:



The intermediate $M(\text{COR})$ is the same as that for carbon monoxide insertion. It may be a coordinatively unsaturated solvated or unsolvated σ -acyl or, alternatively, a π -acyl. It is of interest that photolysis of MeCOMn(CO)_5 in an Ar matrix at 15°K produces what appears to be a trigonal bipyramidal (C_{3v}) MeCOMn(CO)_4 (209).

By assuming a steady-state concentration of $M(\text{COR})$ in Eq. (32), one obtains for the decarbonylation

$$\frac{d[\text{M}(\text{CO})\text{R}]}{dt} = \frac{k_3 k_4 [\text{M}(\text{COR})\text{CO}]}{k_{-3}[\text{CO}] + k_4} \quad (33)$$

and for the substitution

$$\frac{d[\text{M}(\text{COR})\text{L}]}{dt} = \frac{k_3 k'_4 [\text{M}(\text{COR})\text{CO}][\text{L}]}{k_{-3}[\text{CO}] + k'_4[\text{L}]} \quad (34)$$

Since the term $k_{-3}[\text{CO}]$ is usually very small, Eq. (33) simplifies to

$$\frac{d[\text{M}(\text{CO})\text{R}]}{dt} = k_3 [\text{M}(\text{COR})\text{CO}] \quad (35)$$

Experimentally observed rate laws for the decarbonylation conform to Eq. (35).

When $k'_4[\text{L}] \gg k_{-3}[\text{CO}]$ —a condition frequently satisfied—Eq. (34) reduces to

$$\frac{d[\text{M}(\text{COR})\text{L}]}{dt} = k_3 [\text{M}(\text{COR})\text{CO}] \quad (36)$$

and the rate of the decarbonylation equals the rate of ligand substitution. Experimental data for $\text{RCOMn}(\text{CO})_5$ ($\text{R} = \text{Me}$ and Ph) show (Table IV, reactions 1 and 4, and 2 and 5) that the substitution is somewhat faster than the decarbonylation. This presumably arises because the condition that $k_4 \gg k_{-3}[\text{CO}]$ is not strictly fulfilled.

The rate law represented by Eq. (36) also accords with two other mechanistic schemes, illustrated for $\text{MeCOMn}(\text{CO})_5$ [Eqs. (37) and (38)].

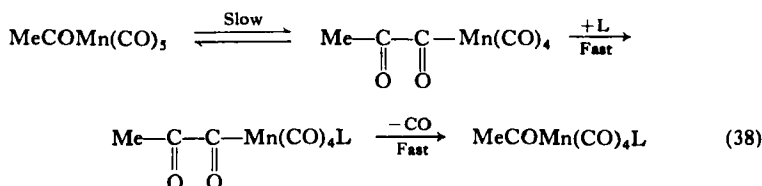
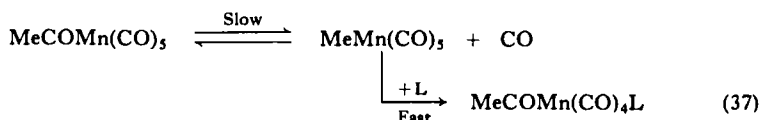


TABLE IV
RATE CONSTANTS FOR DECARBONYLATION AND CO SUBSTITUTION REACTIONS OF MANGANESE(I)

Reaction No.	R	L	Solvent	Temp. (°C)	k_1 (sec ⁻¹)	K (M ⁻¹) ^a	Reference
(a) $\text{RCOMn(CO)}_5 + \text{L} \rightarrow \text{RCOMn(CO)}_4\text{L} + \text{CO}$							
1	Ph	$\text{P(OCH}_2)_3\text{CEt}$	Nitromethane	30.0	23.4×10^{-5}	—	(37)
2	Me	Li^+I^-	2,2'-Diethoxydiethyl ether	30.5	3.2×10^{-5}	—	(54)
(b) $\text{RCOMn(CO)}_5 \rightarrow \text{RMn(CO)}_5 + \text{CO}$							
3	Ph	—	2,2'-Diethoxydiethyl ether	30	22.4×10^{-5}	66	(51)
4	Ph	—	Nitromethane	30.0	13.3×10^{-5}	—	(37)
5	Me	—	2,2'-Diethoxydiethyl ether	30	2.85×10^{-5}	366	(50, 51)
6	Me	—	<i>n</i> -Octyl chloride	30	8.74×10^{-6}	—	(50)
7	Me	—	Mesitylene	30	1.99×10^{-6}	—	(50)
8	Me	—	Dimethylformamide	30	6.61×10^{-6}	—	(50)
9	Et	—	2,2'-Diethoxydiethyl ether	30	3.7×10^{-5}	3300	(51)
10	<i>n</i> -Pr	—	2,2'-Diethoxydiethyl ether	30	5.2×10^{-5}	2700	(51)
11	CH_2Ph	—	2,2'-Diethoxydiethyl ether	30	2.3×10^{-5}	v. small	(51)
(c) $\text{RCOMn(CO)}_4\text{PPh}_3 \rightarrow \text{RMn(CO)}_4\text{PPh}_3 + \text{CO}$							
12	Me	—	<i>n</i> -Hexane	25	3.8×10^{-5}	—	(169)
13	Me	—	THF	25	2.7×10^{-5}	—	(169)

^a Equation (41).

However, the first pathway may be disregarded, since ^{13}C is retained in the acetyl moiety on going from $\text{Me}^{13}\text{COMn}(\text{CO})_5$ to $\text{Me}^{13}\text{COMn}(\text{CO})_4\text{PPh}_3$ (192). Moreover, $\text{PhCOMn}(\text{CO})_5$ reacts considerably (~ 16 times) faster than does $\text{PhMn}(\text{CO})_5$ with $\text{P}(\text{OCH}_2)_3\text{CEt}$ in CHCl_3 at 25°C (37). The second scheme is to be ruled out because $\text{MeCOCOMn}(\text{CO})_5$ decarbonylates 21 times more slowly than $\text{MeCOMn}(\text{CO})_5$ on heating in C_6H_6 at 75°C (60).

2. Effect of Variables

Kinetic studies have been carried out on the decarbonylation of $\text{RCOMn}(\text{CO})_5$



in 2,2'-diethoxydiethyl ether at 30°C (50, 51). Some representative results are included in Table IV. The first-order rate constants (k_3) increase with $\text{R} = \text{CH}_2\text{Ph} < \text{Me} < \text{Et} < n\text{-Pr} < \text{Ph}$, but the spread is only ~ 10 . With the exception of $\text{R} = \text{Ph}$, the above order parallels that for the carbonylation of $\text{RMn}(\text{CO})_5$ (see Section III,D). That the rate constants span such a narrow range is not too surprising, since dissociation of a terminal CO in the rate-determining step need not be greatly influenced by the nature of R in COR. The observed order has been attributed to inductive, mesomeric, and steric effects associated with R.

A study of the reaction



in diethyl ether at 0°C revealed first-order kinetics and a dependence on the nature of R which reflects also both steric and electronic effects (109). Here the rate of CO dissociation varies as $\text{R} = \text{CF}_3$ (0.1) $<$ Me (1) $<$ CH_2Ph (1.3) $<$ Ph (34).

Since the reaction represented by Eq. (39) is reversible, one can ascertain the relative stabilities of the acyls and the corresponding alkyls by examining the values of the equilibrium constants, K [Eq. (41)].

$$K = \frac{[\text{RCOMn}(\text{CO})_5]}{[\text{RMn}(\text{CO})_5][\text{CO}]} \quad (41)$$

Table IV shows that in 2,2'-diethoxydiethyl ether at 30°C , $\text{PhCOMn}(\text{CO})_5$ and, particularly, $\text{PhCH}_2\text{COMn}(\text{CO})_5$ are considerably less stable with

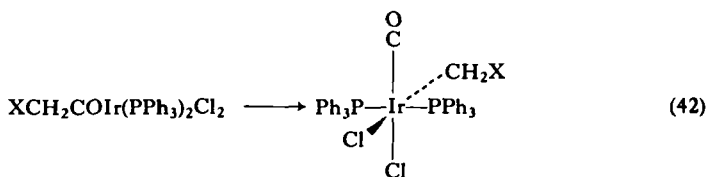
respect to their decarbonylation products than EtCOMn(CO)_5 and $n\text{-PrCOMn(CO)}_5$. However, no similar data are available for other systems.

Solvent effects on the rate of the decarbonylation of MeCOMn(CO)_5 were examined by Calderazzo and Cotton (50) and are presented in part in Table IV. In general they are very small, and no regular trends can be discerned. This virtual lack of dependence of the rate on the nature of the solvent and very little correlation between the rate and the dielectric constant of the solvent are typical of substitution reactions of metal carbonyls (3). In the light of the foregoing, a qualitative observation that $\text{CpFe(CO)}_2\text{-COMe}$ decarbonylates much more readily on treatment at reflux in non-polar heptane or cyclohexane than in polar dioxane is somewhat intriguing (219).

Replacement of CO in MeCOMn(CO)_5 with PPh_3 seems to have little effect on the rate of the decarbonylation. As shown in Table IV, $\text{MeCO-Mn(CO)}_4\text{PPh}_3$ (an isomeric mixture) reacts only slightly faster than MeCOMn(CO)_5 after provision is made for the difference in temperature (169). However, a recent kinetic study on the decarbonylation of $\text{CpMo(CO)}_2\text{L(COMe)}$ (L = a tertiary phosphine) has shown that both inductive and steric properties of L are important (19a). Sterically demanding and weakly σ -bonding phosphines increase the reaction rate.

Also neglected have been kinetic studies concerned with comparison of the rates of the decarbonylation of different M(COR)CO systems. Heck (109) reports that at 25°C MeCOCo(CO)_4 dissociates CO about 2250 times more rapidly than MeCOMn(CO)_5 . This may well be an approximate ratio of the respective rates of the decarbonylation. Qualitative, synthetically oriented experiments seem to indicate that RCOMn(CO)_5 decarbonylate faster than their rhenium counterparts (Section V,C).

Particularly significant is the recently reported kinetic investigation of the reaction (160)



since no loss of ligand occurs in this conversion. Thus, the rate-determining step is the $\text{Ir(COCH}_2\text{X)} \rightarrow \text{Ir(CO)CH}_2\text{X}$ deacylation [Eq. (32), k_4 step] rather than prior dissociation of CO [Eq. (32), k_3 step]. Table V contains

some representative results. They were obtained for X = substituted Ph; the corresponding acetyl and benzoyl complexes rearrange too rapidly to be followed.

It is to be noted that solvent effect on the reaction is rather small; e.g., a 12-fold increase in rate was observed on going from THF to dimethylformamide (Table V, reactions 2 and 4). Addition of pyridine or PPh_3 , which may take up the vacant coordination site in the acyl, slows down the reaction by less than a factor of 2 (Table V, reaction 5). Furthermore,

TABLE V
KINETIC DATA FOR ACYL-ALKYL REARRANGEMENT

Reaction No.	$\text{XCH}_2\text{COIr}(\text{PPh}_3)_2\text{Cl}_2 \rightarrow \text{XCH}_2\text{Ir}(\text{CO})(\text{PPh}_3)_2\text{Cl}_2^a$		Temp. (°C)	k_1 (sec^{-1})	ΔH^\ddagger (kcal/mole)	ΔS^\ddagger (e.u.)
	X	Solvent				
1	Ph	Benzene	35.0	11.9×10^{-4}	17.5	-15.2
2	Ph	Dimethylformamide	35.0	51.2×10^{-4}	—	—
3	Ph	Chloroform	35.0	7.25×10^{-4}	—	—
4	Ph	THF	35.0	4.54×10^{-4}	—	—
5	Ph	Benzene -8.7×10^{-3} pyridine	35.0	7.07×10^{-4}	—	—
6	<i>p</i> - $\text{C}_6\text{H}_4\text{OMe}$	Benzene	35.0	14.1×10^{-4}	15.0	-22.9
7	<i>p</i> - $\text{C}_6\text{H}_4\text{NO}_2$	Benzene	35.0	6.32×10^{-4}	20.2	-7.5
8	C_6F_5	Benzene	40.0	0.68×10^{-4}	—	—

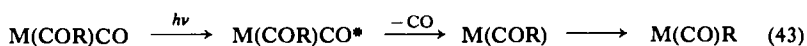
^a From Kubota *et al.* (160).

electron-releasing groups on the phenyl ring promote the rearrangement. However, the effect is not very large, e.g., a 30-fold enhancement for X = *p*- $\text{C}_6\text{H}_4\text{OMe}$ compared to X = C_6F_5 in benzene at 40°C. The small spread may be due to the structural similarity of the compounds examined. The values of ΔH^\ddagger and ΔS^\ddagger decrease from 20.2 kcal/mole and -7.5 e.u. for X = *p*- $\text{C}_6\text{H}_4\text{NO}_2$ to 15.0 kcal/mole and -22.9 e.u. for X = *p*- $\text{C}_6\text{H}_4\text{OMe}$ (Table V, reactions 7 and 6). The authors propose that CH_2X migrates as a carbonium ion-like species onto the vacant coordination site. The varying ΔS^\ddagger values then reflect the positions of the transition state along the reaction coordinate, with the more negative entropy indicating a greater carbonium ion character. However, the carbonium ion formalism is not to be taken literally, since such a species would provide a pathway for racemization at the α -carbon. As shown in Section V, this is not expected to occur.

C. Photolytic Decarbonylation

The ultraviolet light-induced decarbonylation has been successfully effected in several types of transition metal acyl. It is particularly important when applied to those systems which do not eliminate CO under thermal conditions, e.g., $\text{CpFe}(\text{CO})_2\text{COR}$ (141). Most of the work has been of a synthetic rather than mechanistic variety, however.

It is believed that the primary step involves excitation of the acyl complex via a metal-to-terminal CO charge transfer (155). The molecule then loses CO and rearranges to the carbonyl alkyl, as shown in Eq. (43). However, it

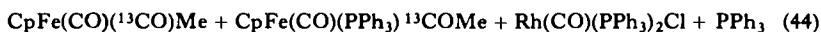
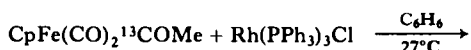


remains to be demonstrated that a terminal rather than the acyl CO is eliminated in these photochemical processes.³

D. Chemical Decarbonylation

In some instances the decarbonylation can be effected, under mild conditions, by using a stoichiometric amount of a CO-abstracting metal complex. This method has proved to be fruitful for several $\text{CpFe}(\text{CO})_2\text{COR}$ compounds (1, 2, 2a) and for $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{COPh}$ (189) in conjunction with $\text{Rh}(\text{PPh}_3)_3\text{Cl}$.

An infrared spectral examination (1) of the products of the reaction



revealed that the acyl-to-alkyl conversion occurs with loss of a terminal and not the ketonic CO. As may be noted in Eq. (44), a major side reaction is ligand substitution. This reflects formation of a common, coordinatively unsaturated intermediate which is captured competitively by PPh_3 and the rearranging R group [see Eq. (32)]. The decarbonylation has been shown to

³ Photochemical decarbonylation of $\text{CpFe}(\text{CO})_2^{13}\text{COMe}$ has now been shown to afford $\text{CpFe}(\text{CO})(^{13}\text{CO})\text{Me}$ which is consistent with loss of a terminal CO [J. J. Alexander, private communication (April 1972)].

prevail with $\text{CpFe}(\text{CO})_2\text{COCH}(\text{Me})\text{Ph}$, whereas exclusive phosphine substitution occurs in $\text{CpMo}(\text{CO})_3\text{COCF}_3$. Other acyl complexes tested yield varying amounts of both types of product. This diverse behavior provides some insight concerning the relative values of k_4 and k'_4 in Eq. (32) for the compounds examined.

Although $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ has been the only decarbonylating reagent employed to date, other platinum metal complexes may prove to be equally, if not more effective. Still to be tested are $\text{Ru}(\text{II})$, $\text{Pt}(0)$, $\text{Pd}(0)$, and other $\text{Rh}(\text{I})$ compounds, to mention a few.

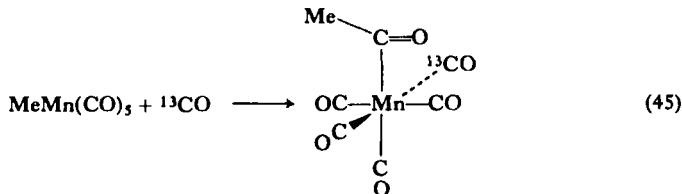
V

STEREOCHEMISTRY OF CARBONYLATION AND DECARBONYLATION

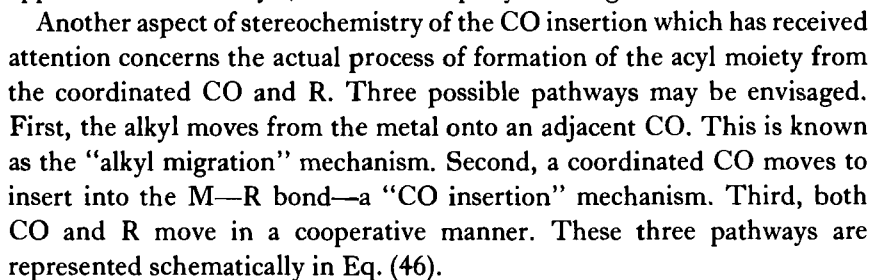
The intramolecular nature of carbon monoxide insertion is demonstrated by the ability of ligands L other than CO to convert an alkyl metal carbonyl to the corresponding acyl complex [Eq. (8)]. As further evidence, when $L = \text{CO}$, the origin of CO in the COR moiety—whether from the parent complex or L —has been established by using labeled carbon monoxide. Coffield *et al.* (29), by employing ^{14}CO in conjunction with $\text{MeMn}(\text{CO})_5$, were able to prove that the incoming CO occupies a terminal position [see Eq. (4)]. This finding was later corroborated by infrared spectroscopy with ^{13}CO (191). More recently, it was found to hold also for $\text{PhCH}_2\text{Co}(\text{CO})_3\text{-PPh}_3$ (177). As expected from the principle of microscopic reversibility, thermal decarbonylation of $\text{Me}^{13}\text{COMn}(\text{CO})_5$ yields $\text{MeMn}(\text{CO})_4(^{13}\text{CO})$ (191). The decarbonylation of $\text{CpFe}(\text{CO})_2^{13}\text{COMe}$ with $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ to give, *inter alia*, $\text{CpFe}(\text{CO})(^{13}\text{CO})\text{Me}$ was discussed in Section IV,D.

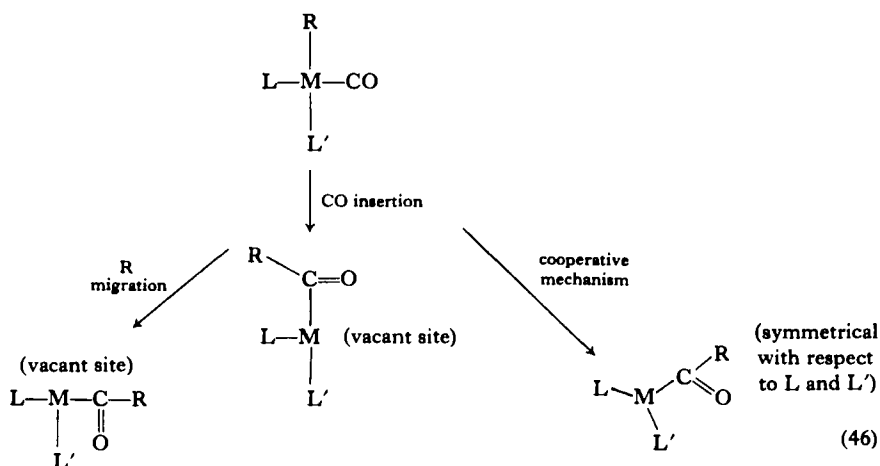
A stereochemical point of considerable interest concerns the position of entry of L with respect to the newly formed acyl moiety. This has been investigated for $\text{RMn}(\text{CO})_5$ and $\text{CpMo}(\text{CO})_3\text{R}$.

An infrared spectral examination of the product of the reaction

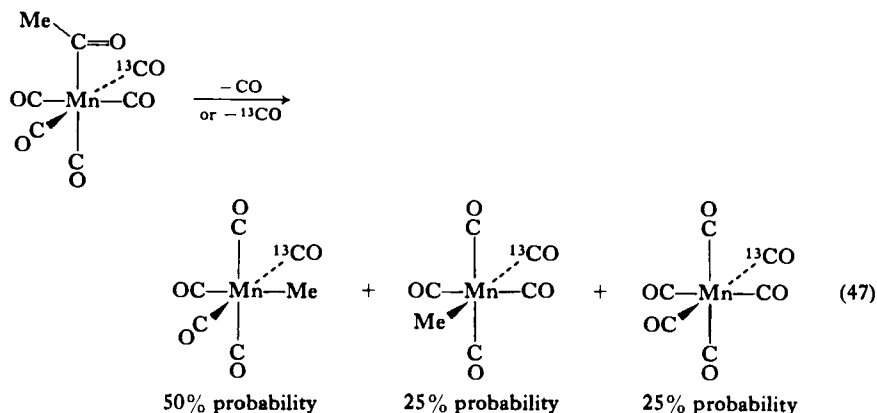


Reactions of $\text{CpMo(CO)}_3\text{R}$ with L also yield products in which COR and L occupy closest possible positions. Thus, $\text{CpMo(CO)}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ and PPh_3 [Eq. (18)] afford the cis product (X) which then isomerizes to the

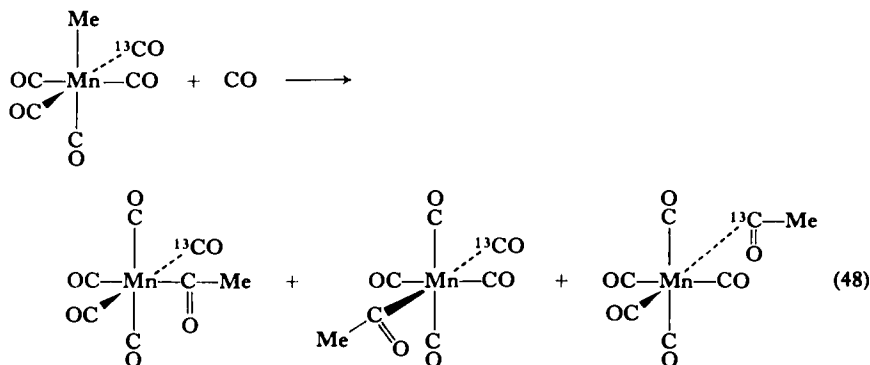




The original claim (169) that the decarbonylation of $\text{MeCOMn}(\text{CO})_4\text{PPh}_3$ to *cis*- $\text{MeMn}(\text{CO})_4\text{PPh}_3$ proceeds via methyl migration was later shown to be inconclusive (156). This is because *cis*- and *trans*- $\text{MeCOMn}(\text{CO})_4\text{PPh}_3$ equilibrate rather rapidly in solution during CO elimination. However, Noack and Calderazzo (191) subsequently demonstrated that decarbonylation of *cis*- $\text{MeCOMn}(\text{CO})_4(^{13}\text{CO})$ gives *cis*- and *trans*- $\text{MeMn}(\text{CO})_4(^{13}\text{CO})$ in the ratio 2:1, consistent with the mechanism of methyl migration onto the site of dissociated CO [Eq. (47)]. The reverse of the mechanism of carbon monoxide insertion would have given exclusively the *cis* isomer, and a symmetrical cooperative process would have afforded a higher proportion of the *cis*- to the *trans*-alkyl, the exact ratio depending on the structure of the reaction intermediate.

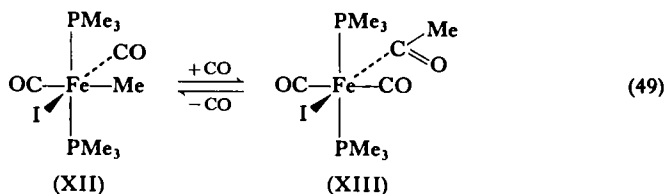


In further support of the alkyl migration, the reaction



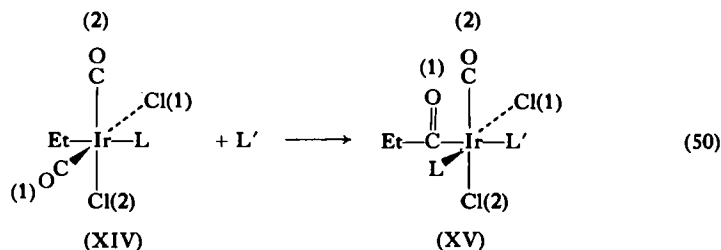
affords the *cis*, *trans*, and $^{13}\text{COMe}$ acetyls in the ratio 2:1:1. Carbonyl insertion would not have yielded the *trans* isomer, whereas a cooperative pathway would have increased the above ratio of the *cis* to the *trans* isomer.

The stereochemistry of the forward and the reverse reaction (200)



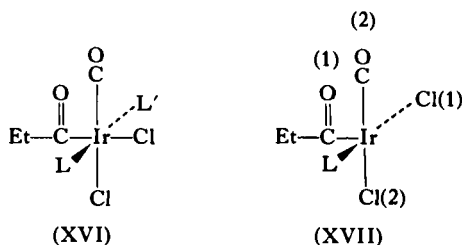
also supports methyl migration. However, the possibility that either (XII) or (XIII) (whose structures were assigned on the basis of their infrared spectra and dipole moments) are secondary, thermodynamically stable, products cannot be completely dismissed.

For the recently reported carbon monoxide insertion reaction (94)



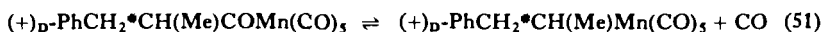
where $\text{L} = \text{AsMe}_2\text{Ph}$ and $\text{L}' = \text{AsMePh}_2$, the hypothesis of alkyl migration does not account for the spectroscopically inferred structure of (XV).

Complex (XV), which isomerizes to (XVI) in a subsequent, slower step, almost certainly is the kinetic product. Its stereoselective formation from

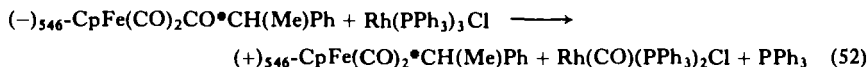


(XIV) and L' [Eq. (50)] may be best rationalized on the basis of the intermediacy of square-pyramidal (XVII), which arises from (XIV) via a concerted approach of Et and CO(1), accompanied by the opening of the Cl(1)—Ir—L bond angle.⁴ It is entirely possible that this mechanism of cooperative migration may be as general, if not more so, than that of alkyl migration.

A complete description of stereochemistry of the carbon monoxide insertion and decarbonylation requires knowledge of configurational changes at the metal and α -carbon. Calderazzo and Noack (54) showed that the optical activity of the equilibrium mixture



does not change with time. Therefore, the forward and the back reaction, both relatively fast, are stereospecific. Similarly, the decarbonylation (2)

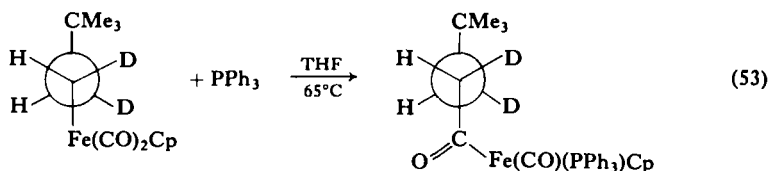


was found to proceed with retention of optical activity, although it could not be determined whether this corresponds to retention or inversion at α -carbon.

The latter question was resolved recently by examination of the NMR

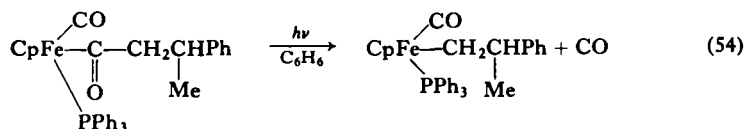
⁴ Additional results indicate that the formation of (XV) is the result of the fact that 5-coordinate Ir(III) complexes prefer a square-pyramidal geometry with the vacant octahedral site trans to the most strongly *trans*-labilizing ligand (COEt) [R. J. Mawby, private communication (March 1972)].

spectrum of the diastereomeric (owing to asymmetric iron) products of the reaction:



The *threo* alkyl yields exclusively (>95%) the *threo* acyls, indicating retention of configuration at carbon (237). Retention was also observed for the carbonylation of palladium-bicyclo[2.2.1]heptadiene complexes to saturated carboxylic esters in the presence of alcohol (218, 131a). These reactions no doubt proceed through formation of Pd—C σ -bonds, carbon monoxide insertion into them, and cleavage of the resulting Pd—C (acyl) linkages. And finally, Rh(PPh₃)₃Cl-promoted decarbonylation of several optically active aldehydes, R'R'C*CHO, was shown generally to be highly stereoselective, taking place with retention of configuration (236).

There has been only one study concerned with stereochemical changes at an asymmetric metal. It dealt with the photochemical decarbonylation (208):



Both the alkyl and the acyl have two asymmetric centers: the iron and the β -carbon. Accordingly, each composition exists as a pair of racemic mixtures. When the two diastereomeric racemic mixtures of the acyl are separately subjected to the decarbonylation in Eq. (54), only partial (<50%) epimerization is observed by NMR spectroscopy. This indicates that in the reactive intermediate, presumably three-coordinate CpFe(PPh₃)COCH₂-CH(Me)Ph, the iron substantially retains its asymmetry, and is therefore not planar.

VI

SURVEY OF REACTIONS

The known CO insertion and decarbonylation reactions are surveyed in this section. Kinetic and stereochemical results already discussed in Sections II–IV have been given a cursory mention for the sake of completeness. Not comprehensively covered are processes which likely proceed via

CO insertion (as inferred from the nature of products), but in which the actual insertion or decarbonylation step has received at most peripheral attention. This particularly applies to industrial carbonylation processes such as hydroformylation. The interested reader is referred to several excellent articles on these subjects (30, 32, 62, 117, 198a, 203a, 228).

Reactions of metal carbonyls with alkyllithium reagents to give the corresponding acyls, e.g., conversion of $\text{W}(\text{CO})_6$ to $\text{Li}[\text{PhCOW}(\text{CO})_5]$ with LiPh (90), undoubtedly involve attack of LiR upon coordinated CO. Another carbanion-like interaction with a bonded CO is thought to be responsible for the formation of



from $\text{Ru}(\text{CO})_3[\text{P}(\text{OMe})_3]_2$ and $\text{CF}_3\text{C}\equiv\text{CCF}_3$ (47). Such reactions are excluded, as are also all aspects of the chemistry of acyl metal complexes other than the carbon monoxide insertion and elimination.

A. Titanium and Vanadium Triads

No CO insertion or decarbonylation studies have been reported for these elements. However, the recent preparation of several stable alkyls (243) may provide some impetus for such investigations.⁵

B. Chromium Triad

1. Chromium

Attempts at the carbonylation of $\text{CpCr}(\text{NO})_2\text{Me}$ in hexane or THF at reflux resulted only in recovery of the nitrosylalkyl (105). A recent report of the reaction between $\text{CpCr}(\text{CO})_3\text{Me}$ and L [$\text{L} = \text{PPh}_3$, $\text{P}(p\text{-C}_6\text{H}_4\text{OMe})_3$, and PMe_2Ph] to yield *trans*- $\text{CpCr}(\text{CO})_2\text{L}(\text{COMe})$ furnishes the first example of insertion of CO into $\text{Cr}-\text{C}$ bonds (196).

2. Molybdenum

The alkyls investigated have been principally of the type $\text{CpMo}(\text{CO})_3\text{R}$, their dicarbonyl substitution products, and π -indenyl analogs.

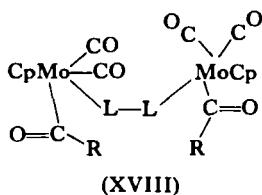
High-pressure carbonylation of $\text{CpMo}(\text{CO})_3\text{R}$ yields the very unstable acyls. The acetyl was detected by infrared spectroscopy but not isolated (70), whereas the propionyl decomposes readily to $[\text{CpMo}(\text{CO})_3]_2$ (172).

⁵ Insertion of CO into $\text{Ti}-\text{C}$ bonds has very recently been reported for reaction of $\text{Cp}_2\text{Ti}(\text{CH}_2\text{Ph})_2$ with CO and for oxidative additions of MeI and EtI to $\text{Cp}_2\text{Ti}(\text{CO})_2$. See refs. (89a) and (90a), respectively.

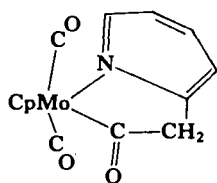
The reaction between $\text{CpMo(CO)}_3\text{Et}$ and CO at $80^\circ\text{--}100^\circ\text{C}$ and 100 atm affords also $[\pi\text{-EtC}_5\text{H}_4\text{Mo(CO)}_3]_2$ (172).

Carbonylation of $\text{CpMo(CO)}_3\text{R}$ with various C and P donor ligands (L) has afforded a series of $\text{CpMo(CO)}_2\text{L(COR)}$ complexes. These reactions can usually be carried out at room temperature in a polar solvent such as MeCN. At higher temperatures, decarbonylation to $\text{CpMo(CO)}_2\text{LR}$ may become noticeable. Prepared in this manner have been the following: $\text{CpMo(CO)}_2\text{L(COMe)}$ [$\text{L} = \text{PPh}_3$ (18, 20, 100); PEt_3 (56); $\text{P}(n\text{-Bu})_3$, P(OPh)_3 (18); P(OMe)_3 (18, 56); Tdp (17, 56); $\text{P}(n\text{-OBu})_3$ (48); Me_3CNC , and $2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC}$ (245)], $\text{CpMo(CO)}_2\text{L(COEt)}$ [$\text{L} = \text{PPh}_3$, $\text{P}(n\text{-Bu})_3$, P(OMe)_3 , P(OEt)_3 , P(OPh)_3 , and $\text{P(OCH}_2)_3\text{CMe}$] (80), $\text{CpMo(CO)}_2\text{-L(COCH}_2\text{CH=CH}_2)$ [$\text{L} = \text{PPh}_3$ and $\text{P(OCH}_2)_3\text{CEt}$] (81), $\text{CpMo(CO)}_2\text{-L(COCH}_2\text{Ph)}$ [$\text{L} = \text{PPh}_3$, $\text{P}(n\text{-Bu})_3$, P(OPh)_3 , $\text{P(OCH}_2)_3\text{CEt}$ (81), and Me_3CNC (245)], $\pi\text{-C}_9\text{H}_7\text{Mo(CO)}_2\text{L(COMe)}$ [$\text{L} = \text{PPh}_3$, P(OMe)_3 , and P(OPh)_3] (108), and $\pi\text{-(MeO)}_2\text{C}_9\text{H}_5\text{Mo(CO)}_2[\text{P(OMe)}_3]\text{COMe}$ (108). The reaction of $\text{CpMo(CO)}_3(\text{CH}_2\text{C}_6\text{H}_4\text{X-}p)$ with $\text{C}_6\text{H}_{11}\text{NC}$ [Eq. (5)] yields both $\text{CpMo(CO)}_2(\text{C}_6\text{H}_{11}\text{NC})(\text{COCH}_2\text{C}_6\text{H}_4\text{X-}p)$ and $\text{CpMo(CO)}_3[\text{C}(\text{CH}_2\text{C}_6\text{H}_4\text{X-}p)=\text{NC}_6\text{H}_{11}]$, the amount of the latter product increasing with the electron-withdrawing ability of X in the order: OMe (40%) < H (51%) < Cl (72%) (246). The ionic $\text{K}[\text{CpMo(CO)}_2(\text{CN})\text{COMe}]$ was prepared by treatment of $\text{CpMo(CO)}_3\text{Me}$ with KCN (158a).

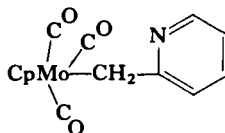
Treatment of $\text{CpMo(CO)}_3\text{R}$ with bidentate P donor ligands (L—L) affords the following: $[\text{CpMo(CO)}_2\text{COR}]_2(\text{L—L})$ (XVIII) [$\text{R} = \text{Me}$ or CH_2Ph , $\text{L} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (20, 147), $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$, and *trans*- $\text{Ph}_2\text{PCH=CHPPh}_2$ (147)] and $[\text{CpMo(CO)}_2\text{COMe}]_2(\text{L—L})$ [$\text{L—L} = \text{Ph}_2\text{PC}\equiv\text{CPPh}_2$ (147) and $\text{Ph}_2\text{PCH}_2\text{C}\equiv\text{CCH}_2\text{PPh}_2$ (145)]. The reaction between $\text{CpMo(CO)}_3\text{R}$ ($\text{R} = \text{Me}$ or CH_2Ph) and *cis*- $\text{Ph}_2\text{PCH=CHPPh}_2$ (L—L) in MeCN yields $\text{Mo(CO)}_2(\text{L—L})_2$ instead (147).



Iodide (48), $\text{As(OCH}_2)_3\text{CMe}$, $\text{S}(t\text{-Bu})_2$ (79), and pyridines (80) do not react with $\text{CpMo(CO)}_3\text{Me}$ in THF or MeCN. However, interaction between $\text{Na}[\text{CpMo(CO)}_3]$ and 2-(chloromethyl)pyridine has afforded (XIX) (144),

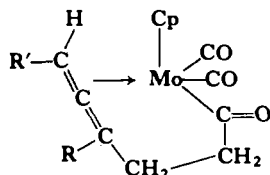


(XIX)



(XX)

no doubt via the intermediacy of (XX). When $\text{Na}[\text{CpMo}(\text{CO})_3]$ and $\text{Br}(\text{CH}_2)_2\text{C}(\text{R})=\text{C}=\text{CHR}'$ ($\text{R} = \text{R}' = \text{H}$; $\text{R} = \text{H}$, $\text{R}' = \text{Me}$; $\text{R} = \text{Me}$, $\text{R}' = \text{H}$) are heated in THF, novel π -allene acyl complexes (XXI) result (23).



(XXI)

Their precursors must be the tricarbonyl σ -allenyls with the uncoordinated $\text{C}=\text{C}$ bonds. Neither an allylic rearrangement nor cis-trans isomerization has been observed in the reaction of $\text{CpMo}(\text{CO})_3(\text{cis-CH}_2\text{CH}=\text{CHMe})$ with PPh_3 , the product being $\text{CpMo}(\text{CO})_2(\text{PPh}_3)(\text{cis-COCH}_2\text{CH}=\text{CHMe})$ (81). The interesting reaction leading to the formation of cationic carbene compounds was mentioned earlier [Eq. (17) and Section V] (78).

Insertion of CO into Mo—C bonds has been postulated in the reaction



catalyzed by $[\text{CpMo}(\text{CO})_3]_2$ (221).

Kinetic studies have been made of the reaction of $\text{CpMo}(\text{CO})_3\text{R}$ ($\text{R} = \text{Me}$, Et , CH_2Ph , and $\text{CH}_2\text{CH}=\text{CH}_2$) (48, 80, 81) and $\pi\text{-X}_2\text{C}_6\text{H}_5\text{Mo}(\text{CO})_3\text{Me}$ ($\text{X} = \text{H}$ or OMe) (108) with a variety of P donor ligands L. Solvents employed ranged from nonpolar hexane to polar THF and MeCN. Generally, the mechanism is very sensitive to the coordinating ability of the solvent and the nucleophilicity of L.

Unlike the parent tricarbonyls, complexes of the type $\text{CpMo}(\text{CO})_2\text{LR}$ do not appear to undergo CO insertion. Attempts at the carbonylation of $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{Me}$ under 78 atm of CO were unsuccessful (17); passing CO through a solution of the dicarbonyl in THF at reflux afforded only some $\text{CpMo}(\text{CO})_3\text{Me}$ (20).

The decarbonylation of the perfluoroacyl complexes $\text{CpMo}(\text{CO})_3\text{COR}_\text{F}$ ($\text{R}_\text{F} = \text{CF}_3$ and C_3F_7) and $[\text{CpMo}(\text{CO})_3]_2[\text{CO}(\text{CF}_2)_3\text{CO}]$, which are much more stable than their hydrocarbon counterparts, can be effected by heating at $115^\circ\text{--}130^\circ\text{C}$ (141). However, an attempted elimination of the acyl CO from $\text{CpMo}(\text{CO})_3\text{COCF}_3$ with $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ gave only $\text{CpMo}(\text{CO})_2\text{-(PPh}_3\text{)COCF}_3$ (1).

Complexes of formula $\text{CpMo}(\text{CO})_2\text{L(COR)}$ decarbonylate readily to $\text{CpMo}(\text{CO})_2\text{LR}$ on heating. Occasionally $\text{CpMo}(\text{CO})_3\text{R}$ is also produced in these reactions, perhaps via migration of R with displacement of L. Thus, $\text{CpMo}(\text{CO})_2\text{L(COMe)}$ [$\text{L} = \text{PPh}_3$ (20) and Tdp (17)] on heating in THF yield both the dicarbonyl alkyl and the tricarbonyl acyl. However, decarbonylation in CD_3CN at 60°C of the acetyls with $\text{L} = \text{PPh}_3$, P(OPh)_3 , P(OMe)_3 , and $\text{P}(n\text{-Bu)}_3$ is reported to give only the corresponding dicarbonyl methyl complexes (18). The $\text{L} = \text{PPh}_3$ acetyl of a *trans* configuration yields the *trans* product. Photochemical CO elimination from *cis,trans*- $\text{CpMo}(\text{CO})_2(\text{CNCMe}_3)\text{COCH}_2\text{Ph}$ affords the *trans*-alkyl (245). The complex $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{COPh}$, which undergoes destruction in THF at reflux, has been successfully decarbonylated with $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ (189).

Recently a kinetic study has been reported of the decarbonylation of various $\text{CpMo}(\text{CO})_2\text{L(COMe)}$ ($\text{L} = \text{a tertiary phosphine}$) to $\text{CpMo}(\text{CO})_2\text{-LMe}$ (19a).

3. Tungsten

Reactions of $\text{CpW}(\text{CO})_3\text{R}$ with various ligands proceed much more slowly than those of $\text{CpMo}(\text{CO})_3\text{R}$. Apart from one report—that $\text{CpW}(\text{CO})_3\text{Me}$ reacts with PEt_3 to give $\text{CpW}(\text{CO})_2(\text{PEt}_3)\text{COMe}$ (experimental conditions were not provided) (56)—no CO insertion had been observed until 1972 (*vide infra*). Instead, reactions of $\text{CpW}(\text{CO})_3\text{Me}$ with PPh_3 or $\text{Ph}_2\text{PC}\equiv\text{CPh}_2$ under forcing conditions have yielded only $\text{CpW}(\text{CO})_2\text{-(PPh}_3\text{)Me}$ (20) and $[\text{CpW}(\text{CO})_2\text{Me}]_2(\text{Ph}_2\text{PC}\equiv\text{CPh}_2)$ (147), respectively, via an unknown mechanism. The former product is also obtainable, in better yields, photochemically (20). Treatment of $\text{CpW}(\text{CO})_3\text{COMe}$ with PPh_3 in THF at reflux affords trace quantities of $\text{CpW}(\text{CO})_3\text{Me}$ and $\text{CpW}(\text{CO})_2(\text{PPh}_3)\text{COMe}$ (17), but their origin has not been explored.

Recently it has been reported that the reaction between $\text{CpW}(\text{CO})_3\text{Me}$ and KCN yields $\text{K}[\text{CpW}(\text{CO})_2(\text{CN})\text{COMe}]$ (158a).

Unlike some of their molybdenum analogs, $\text{CpW}(\text{CO})_3\text{COR}$ ($\text{R} = \text{CF}_3$, C_3F_7 , and $\text{CH}=\text{CH}_2$) do not lose CO on sublimation (141). However,

decarbonylation of the last compound has been observed in the mass spectrometer (140).

C. Manganese Triad

1. Manganese

Complexes of the type $\text{RMn}(\text{CO})_5$, where R is a primary alkyl group, undergo facile CO insertion at room temperature. Carbonylated to the corresponding acyls have been the pentacarbonyls with R = Me (50, 69), Et (51, 70), *n*-Pr (51), and CH_2SiMe_3 (243). The phenyl compound, $\text{PhMn}(\text{CO})_5$, also inserts CO, but the benzyl analog does not (51). The claim (194) that $\text{CX}_3\text{Mn}(\text{CO})_5$ (X = H, D, or F) converts to $\text{CX}_3\text{COMn}(\text{CO})_n$ ($n < 5$) upon irradiation in an Ar matrix at 17°K has been disputed (209). Carbon monoxide dissociation and recombination have been proposed instead for $\text{MeMn}(\text{CO})_5$.

A large number of $\text{RCOMn}(\text{CO})_5$ complexes have been decarbonylated [Eq. (39)]. They include the acyls with R = Me (50, 69), Et, *n*-Pr (51), CH_2Ph (69), $\text{CH}_2\text{CH}(\text{Me})\text{Ph}$ (54), and Ph (51, 70), all of which lose CO on storage in solution. Also decarbonylated, but principally with a view to synthesizing the corresponding alkyls, have been the following: R = CF_3 (22, 70, 171), C_2F_5 (135), *n*- C_3F_7 , *i*- C_3F_7 , $(\text{CF}_2)_4\text{Cl}$, $(\text{CF}_2)_4\text{H}$ (171), $(\text{CF}_2)_2\text{H}$ (226), *p*- $\text{C}_6\text{H}_4\text{OMe}$, *p*- $\text{C}_6\text{H}_4\text{F}$ (193), *p*- $\text{C}_6\text{H}_4\text{X}$ (X = Cl, Br, and I) (182), *m*- and *p*- $\text{C}_6\text{H}_4\text{CN}$, *m*- and *p*- $\text{C}_6\text{H}_4\text{CF}_3$, *m*- $\text{C}_6\text{H}_4\text{X}$ (X = F, Cl, and Br) (217), $(\text{CH}_2)_2\text{CO}_2\text{Me}$ (178), 2-furyl (179), 5-methyl-2-furyl, 2-thienyl, benzofuryl (180), and COMe (60). Heating $[\text{Mn}(\text{CO})_5](\text{CORCO})$ at $>100^\circ\text{C}$ has afforded bimetallic alkyls with R = $(\text{CF}_2)_3$ (139), *m*- C_6H_4 (181), and *p*- C_6H_4 (178, 181). Another decarbonylation is that occurring in the synthesis of $(2\text{-C}_4\text{H}_3\text{S})\text{Mn}(\text{CO})_5$ from $2\text{-ClCOC}_4\text{H}_3\text{S}$ and $\text{NaMn}(\text{CO})_5$ (207). No decarbonylation of $\text{CprCOMn}(\text{CO})_5$ could be effected either thermally or photolytically (44). On heating, $\text{ClCH}_2\text{COMn}(\text{CO})_5$ decomposes to unidentified products (55), and *o*- $\text{MeC}_6\text{H}_4\text{COMn}(\text{CO})_5$ yields $\text{Mn}_2(\text{CO})_{10}$ (184).

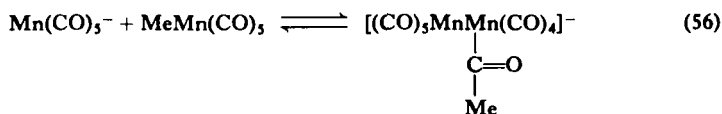
Complexes of formula $\text{MeCOMn}(\text{CO})_4\text{L}$ with L = SbPh_3 , AsPh_3 , or a P donor ligand lose CO either spontaneously on storage or on warming to afford *cis*- $\text{MeMn}(\text{CO})_4\text{L}$ (157). However, the corresponding amine (157) or iodo (136) acyls could not be decarbonylated. Perfluoroacylmanganese tricarbonyls readily undergo the decarbonylation on heating. Thus, thermolysis ($60^\circ\text{--}130^\circ\text{C}$) of $\text{CF}_3\text{COMn}(\text{CO})_3\text{L}_2$ [L = PPh_3 or P(OPh)_3]

and $\text{C}_2\text{F}_5\text{COMn}(\text{CO})_3(\text{PPh}_3)_2$ has yielded the corresponding alkyls. By contrast, loss of the acyl CO occurs spontaneously when $\text{Mn}(\text{CO})_3[\text{P}(\text{OPh})_3]_2^-$ is treated with $(\text{C}_2\text{F}_5\text{CO})_2\text{O}$ (129). Unfortunately, these data do not permit a generalization concerning the relative ease of CO elimination from $\text{RCOMn}(\text{CO})_5$ and the analogous $\text{RCOMn}(\text{CO})_3\text{L}_2$.

The reactions of $\text{RMn}(\text{CO})_5$ with a large variety of ligands other than CO have been the subject of both synthetic and mechanistic studies. In general, these pentacarbonyls manifest much less selectivity toward different L than do $\text{CpMo}(\text{CO})_3\text{R}$. Thus, formation of $\text{MeCOMn}(\text{CO})_4\text{L}$ is effected by PPh_3 (52, 156); PMePh_2 , PMe_2Ph , PEt_3 , PPh_2H (157); $\text{P}(\text{OCH}_2)_3\text{CMe}$ (99, 157); $\text{P}(\text{OCH}_2)_3\text{CEt}$ (99); $\text{P}(\text{OPh})_3$, $\text{P}(\text{OMe})_3$ (157); AsPh_3 , SbPh_3 (13, 15); $\text{C}_6\text{H}_{11}\text{NH}_2$, $(\text{Me})(\text{C}_6\text{H}_{11})\text{NH}$, PhNH_2 (136, 157); NH_3 (136), I^- ; CN^- , SCN^- , and OMe^- (53). Some of these reactions proceed to completion; in other cases, equilibria are established among *cis*- and *trans*- $\text{MeCOMn}(\text{CO})_4\text{L}$, their decarbonylation product *cis*- $\text{MeMn}(\text{CO})_4\text{L}$, and/or $\text{MeMn}(\text{CO})_5$ (157). For every system examined, *cis*- $\text{MeCOMn}(\text{CO})_4\text{L}$ forms initially in the insertion. The ligands BiPh_3 , PCl_3 , $(\text{C}_6\text{H}_{11})_2\text{NH}$, Ph_2NH , $\text{P}(o\text{-C}_6\text{H}_4\text{Me})_3$ (157), $\text{C}_5\text{H}_5\text{N}$, and Me_3N (136) fail to react, presumably owing to a combination of steric and electronic factors.

The methyl pentacarbonyl reacts also with $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1$ or 2) ($\text{L}-\text{L}$) to afford *fac*- $\text{MeCOMn}(\text{CO})_3(\text{L}-\text{L})$ (158, 170). Each complex decarbonylates to the alkyl of the same stereochemistry (158). A higher ratio of $\text{MeMn}(\text{CO})_5$ to the $n = 2$ ligand in the first reaction results in the formation of $[\text{MeCOMn}(\text{CO})_4]_2(\text{L}-\text{L})$ (170).

The role of L can be also assumed by $\text{Mn}(\text{CO})_5^-$. If the equilibrium mixture (59)



is treated with $\text{Me}_3\text{O}^+\text{BF}_4^-$, a carbene complex, $(\text{CO})_5\text{MnMn}(\text{CO})_4\text{-}[\text{C}(\text{Me})\text{OMe}]$, results. A similar type of structure has recently been proposed for $[\text{Mn}(\text{CO})_5]_2(\text{CH}_2)_3$; it undoubtedly arises through carbon monoxide insertion (58).

Insertion reactions have also been observed for the pentacarbonyls with $\text{R} = \text{CH}_2\text{F}$, effected by $\text{L} = \text{I}^-$ (54), and $\text{R} =$ various aryl groups, by several L. The unstable acyl $\text{PhCOMn}(\text{CO})_4\text{PPh}_3$, formed from $\text{PhMn}(\text{CO})_5$ and

PPh_3 , readily decarbonylates to *cis*- $\text{PhMe}(\text{CO})_4\text{PPh}_3$ (35). Interestingly, treatment of the last-mentioned compound with 250 atm of CO affords $\text{PhCOMn}(\text{CO})_5$ (13). Cyclohexylamine and aniline (RNH_2) react with $\text{PhMn}(\text{CO})_5$ to give the expected $\text{PhCOMn}(\text{CO})_4(\text{RNH}_2)$ (136). A complex series of interrelated carbonylation and decarbonylation reactions occur in systems derived from $\text{PhMn}(\text{CO})_5$ and $\text{P}(\text{OCH}_2)_3\text{CEt}$ (L) (35). Insertion yields *cis*- $\text{PhCOMn}(\text{CO})_4\text{L}$ (which is stable, unlike its $\text{L} = \text{PPh}_3$ counterpart), both *fac*- and *mer*(L's *trans*)- $\text{PhCOMn}(\text{CO})_3\text{L}_2$, and, under forcing conditions, $\text{PhCOMn}(\text{CO})_2\text{L}_3$. Analogous aroyl or aryl tri- and tetracarbonyls have been isolated from reactions of $\text{PhMn}(\text{CO})_5$ with AsPh_3 , SbPh_3 , $\text{P}(\text{OMe})_3$, $\text{P}(\text{OPh})_3$, $\text{P}(\text{OPh})_2\text{Me}$, and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (13, 15).

Aryl complexes bearing a *meta* or a *para* substituent undergo similar reactions. Accordingly, the pentacarbonyls with $\text{R} = m\text{-}$ or $p\text{-C}_6\text{H}_4\text{X}$ ($\text{X} = \text{F}$ or Cl) react with a number of P and As donor ligands and, depending on the conditions, force the formation of aryl or aroyl tetra- or tricarbonyls (4, 217). However, the reaction of $\text{C}_6\text{F}_5\text{Mn}(\text{CO})_5$ with neutral ligands proceeds only with replacement of CO (197).

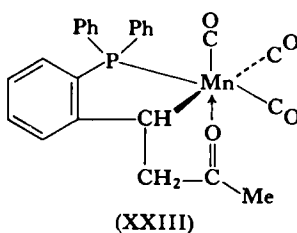
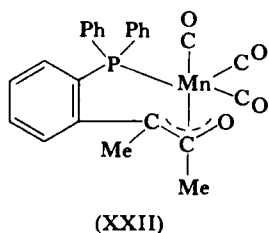
Consistent with its reported inertness to carbonylation (51), $\text{PhCH}_2\text{Mn}(\text{CO})_5$ does not yield an acyl on treatment with $\text{C}_6\text{H}_{11}\text{NH}_2$ (136). The related complex *m*- $\text{FC}_6\text{H}_4\text{CH}_2\text{Mn}(\text{CO})_5$ reacts with neutral mono- and bidentate ligands to furnish substitution products (217).

The reactions of $\text{MeMn}(\text{CO})_5$ with various phosphines and phosphites (L) to give *fac*- $\text{MeCOMn}(\text{CO})_3\text{L}_2$ and/or *mer*(L's *trans*)- $\text{MeCOMn}(\text{CO})_3\text{L}_2$ have been monitored by NMR spectroscopy (166). Sterically demanding L's promote formation of the *meridional* over the *facial* isomer. Interestingly, the *meridional* acetyls decarbonylate more easily than their *facial* counterparts, perhaps owing to a weaker $\text{Mn}-\text{CO}$ bond *cis* to COMe in the former.

When $\text{MeCOMn}(\text{CO})_3\text{L}_2$ and L [$\text{L} = \text{P}(\text{OMe})_3$] are heated under ultraviolet light, the initially formed $\text{MeMn}(\text{CO})_3\text{L}_2$ reacts further to give $\text{MeMn}(\text{CO})_2\text{L}_3$ and $\text{MeMn}(\text{CO})\text{L}_4$ (225). These alkyls undergo CO insertion at 300 psi, yielding $\text{MeCOMn}(\text{CO})_3\text{L}_2$.

Two examples are noteworthy of the chelate effect in the formation of acyl complexes. The reaction of $\text{NaMn}(\text{CO})_5$ with $\text{MeSCH}_2\text{CH}_2\text{Cl}$ at -78°C yields $\text{Me}\overline{\text{SCH}_2\text{CH}_2\text{COMn}(\text{CO})_4}$ (143), the intermediacy of the pentacarbonyl alkyl being a virtual certainty. Similarly, $\text{NaMn}(\text{CO})_5$ and $\text{ClCH}_2\text{CH}_2\text{NMe}_2$ afford $\text{Me}_2\text{N}\overline{\text{CH}_2\text{CH}_2\text{COMn}(\text{CO})_4}$ (144).

Both MeMn(CO)_5 and PhMn(CO)_5 react with acetylenes to yield vinyl ketone tetracarbonyl complexes, most likely via a pathway involving CO insertion [Eq. (18)] (14, 36). Reactions of these same alkyls with 1,3-dienes may proceed similarly (16, 95, 96). The chelating ligand *o*-styryldiphenylphosphine (L-L) converts MeMn(CO)_5 into two products (25) whose structures (XXII and XXIII) were elucidated by X-ray crystallography (24). An unusual migration of COMe onto L-L occurs subsequently to the initial insertion step.



Unexpected types of behavior include formation in small amounts of $\text{Mn}_2(\text{CO})_9\text{CNPh}$ and $\text{Mn}_2(\text{CO})_8(\text{CNPh})_2$ from RMn(CO)_5 ($\text{R} = \text{Me}$ or Ph) and PhNC (134), and phosphine replacement by CO in $\text{MeMn(CO)}_4\text{-Tdp}$ to give MeMn(CO)_5 (150).

Kinetic (37, 50–52, 97, 168) and stereochemical (54, 191, 192) investigations on the carbonylation of manganese alkyls and the decarbonylation of manganese acyls were already discussed in Sections III–V. The original finding (50) that the rate of CO insertion follows second-order kinetics has now been qualified (192). At higher pressures of CO (>15 atm) the first-order rate law [Eq. (23)] is obeyed.

2. Rhenium

Little work has been done with analogous compounds of rhenium. Treatment of $p\text{-ClC}_6\text{H}_4\text{Re(CO)}_5$ with PPh_3 at $50^\circ\text{--}60^\circ\text{C}$ yields *cis-p*- $\text{ClC}_6\text{H}_4\text{Re(CO)}_4\text{PPh}_3$ by an unknown pathway. The same product results from $p\text{-ClC}_6\text{H}_4\text{COPh(CO)}_5$ and PPh_3 ; the decarbonylation followed by ligand substitution has been proposed. The reaction of $m\text{-ClC}_6\text{H}_4\text{COPh(CO)}_5$ with PPh_3 proceeds similarly (4).

Acylrhenium pentacarbonyls lose CO on heating, but generally at temperatures $30^\circ\text{--}70^\circ\text{C}$ higher than those required for the corresponding RCOMn(CO)_5 . The following RCOPh(CO)_5 have been decarbonylated: $\text{R} = \text{Me}$, Ph (127); C_2F_5 , C_3F_7 (135); C_6F_5 (133); *m*- and *p*- $\text{C}_6\text{H}_4\text{Me}$ (184);

p-C₆H₄X (X = Cl, Br, and I) (182); *o*- and *m*-C₆H₄Cl (183); and *o*-RCB₁₀H₁₀C (R = Me or Ph) (248). The bimetallic [Re(CO)₅]₂(CORCO) (R = *m*- and *p*-C₆H₄) lose two CO's on heating to afford the corresponding aryl complexes (181). Thermolysis of *o*-MeC₆H₄CORe(CO)₅ produces Re₂(CO)₁₀ (184). No decarbonylation of CpRe(CO)₅ could be effected either thermally or photolytically (44).

D. Iron Triad

1. Iron

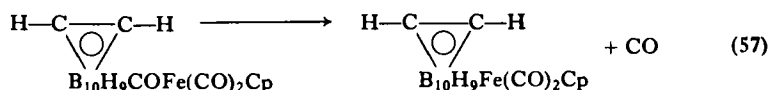
Most of the investigations have dealt with CpFe(CO)₂R and their monosubstitution products.

Carbonylation of CpFe(CO)₂Me at 125°C and 2000 psi of CO has afforded CpFe(CO)₂COMe [Eq. (2)] (70), which, unlike CpMo(CO)₃COMe, is stable. No other analogous acyls have been prepared by this method, almost certainly because of the availability of a more convenient synthesis from Na[CpFe(CO)₂] and RCOCl.

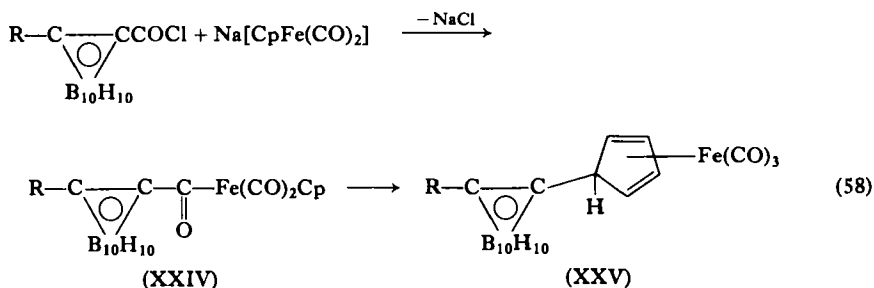
Acyl complexes of the type CpFe(CO)₂COR resist thermal decarbonylation, a behavior contrasting with that of their molybdenum tricarbonyl counterparts. Thus, [CpFe(CO)₂]₂[CO(CX₂)₃CO] (X = H or F) remains unchanged after thermolysis at 130°C (138). These compounds can, however, be converted to the corresponding alkyls by the application of ultraviolet light. The decarbonylation has been effected in this manner for CpFe(CO)₂COR with R = Me, Ph, CH=CH₂ (141); *p*-C₆H₄F (217); CF₃, C₂F₅, and C₃F₇ (141); as well as for [CpFe(CO)₂][CO(CF₂)₃CO] (141), but not for CpFe(CO)₂COCpr (44). In many cases it furnishes the best known synthesis of the alkyl. Successful elimination of CO has also been achieved by using Rh(PPh₃)₃Cl as the decarbonylating agent. This reagent affords the alkyls with R = CH(Me)Ph (1), Me, and Ph (2). In the reaction of the last two acyls, CpFe(CO)(PPh₃)COR is produced as well. A facile decarbonylation of CpFe(CO)₂COPh has been observed in the mass spectrometer (140).

An interesting reaction has been reported between CpFe(CO)₂⁻ and C₆F₅COCl (33). The products are CpFe(CO)₂C₆F₅, CpFe(CO)₂C₆F₄H-*p*, and CpFe(CO)₂C₆F₄COFe(CO)₂Cp. The bimetallic acyl surprisingly yields a small amount of CpFe(CO)₂C₆F₄H-*p* on photolysis, there being no evidence for the expected CpFe(CO)₂C₆F₄Fe(CO)₂Cp.

A compound with an Fe—B bond is formed by the novel decarbonylation (249):



The starting material results from the reaction of 3-*o*-carboranecarboxylic acid chloride with Na[CpFe(CO)₂]. Similarly, the first step of the reaction



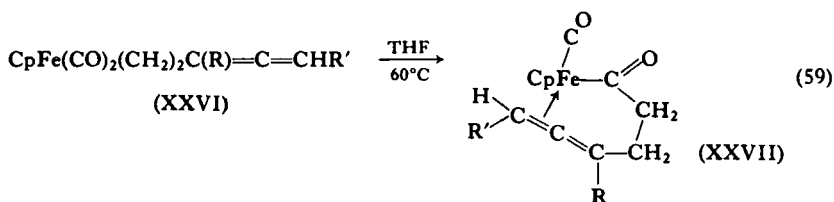
(250) affords isolable (XXIV), together with (XXV), when R = H. However, when R = Me or Ph, only (XXV) is obtained, presumably via migration of RCB₁₀H₁₀C onto the Cp ring of the precursor (XXIV). Treatment of Na[CpFe(CO)₂] with *m*-HCB₁₀H₁₀CCOCl yields the expected acyl which, on heating, decarbonylates to *m*-HCB₁₀H₁₀CFe(CO)₂Cp. Similarly prepared was *o*-MeCB₁₀H₁₀CH₂COFe(CO)₂Cp; however, it required ultraviolet light for conversion to the alkyl.

The reactions of CpFe(CO)₂R with various ligands L to give CpFe(CO)-L(COR) [Eq. (30)] have been the subject of numerous investigations. Kinetic studies have been reported for the insertion in CpFe(CO)₂Me (48, 98), -Et, and -*i*-Pr (98) effected by various phosphines and phosphites. Noteworthy again is a striking discriminatory effect of L. Apart from relatively few exceptions, presented later, only P donor ligands have been successful in forcing this type of conversion. Reported not to react with or to decompose CpFe(CO)₂Me have been I⁻, SEt₂, *p*-MeC₆H₄NH₂, *p*-ClC₆H₄NH₂, C₅H₅N (28), and C₆H₁₁NH₂ (48)—the types of ligand also inert to CpMo(CO)₃Me. However, RNC (R = C₆H₁₁ and *t*-Bu) and CN⁻ yield CpFe(CO)(CNR)COMe and CpFe(CO)(CN)COR'⁻ (R' = Me and Et) upon reaction with the respective dicarbonyl alkyls (246a, 158a).

Synthetic investigations have, however, dominated this aspect of alkyliron chemistry. Acyl complexes of formula CpFe(CO)L(COMe) have been

prepared from $\text{CpFe}(\text{CO})_2\text{Me}$ by using the following L: PPh_3 (28, 100), $\text{P}(\text{OPh})_3$, $\text{P}(n\text{-Bu})_3$, $\text{P}(n\text{-OBu})_3$ (28); PMe_2Ph (45, 46); and $\text{P}(\text{C}_6\text{H}_{11})_3$ (101). Synthesized similarly, usually in MeCN or THF at reflux, were $[\text{CpFe}(\text{CO})\text{COMe}]_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ (17); $\text{CpFe}(\text{CO})\text{L}(\text{COEt})$ [$\text{L} = \text{PPh}_3$, PMe_2Ph , PMePh_2 , $\text{P}(\text{OMe})_3$, $\text{P}(\text{OPh})_3$, and $\text{P}(n\text{-Bu})_3$], $\text{CpFe}(\text{CO})\text{L}(\text{CO-}i\text{-Pr})$ ($\text{L} = \text{PPh}_3$ and PMe_2Ph) (98); $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{COCH}_2\text{Ph}$ (45, 46); $\text{CpFe}(\text{CO})\text{L}(\text{COCH}_2\text{SiMe}_3)$ ($\text{L} = \text{PPh}_3$, PMePh_2 , and PEtPh_2) (151, 201), and $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{COCHDCHDCMe}_3$ (237).

The interesting π -allene complexes (XXVII; $\text{R} = \text{R}' = \text{H}$; $\text{R} = \text{H}$, $\text{R}' = \text{Me}$; $\text{R} = \text{Me}$, $\text{R}' = \text{H}$) arise by the carbon monoxide insertion (23):



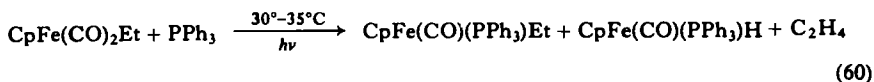
The same product, as well as $\text{CpFe}(\text{CO})[\text{P}(n\text{-Bu})_3]\text{CO}(\text{CH}_2)_2\text{CH}=\text{C}=\text{CHMe}$, is obtainable by treatment of (XXVI; $\text{R} = \text{H}$, $\text{R}' = \text{Me}$) with $\text{P}(n\text{-Bu})_3$ under similar conditions. However, the reaction between $\text{CpFe}(\text{CO})_2\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$ and PPh_3 yields only $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{COCH}_2\text{CH}_2\text{CH}=\text{CH}_2$. Cyclic derivatives similar to (XXVII) result from thermal decomposition of $\text{CpFe}(\text{CO})_2\text{CH}_2\text{CR}_2\text{CH}=\text{CH}_2$ ($\text{R} = \text{H}$ or Me) (103).

Like $\text{NaMn}(\text{CO})_5$, $\text{Na}[\text{CpFe}(\text{CO})_2]$ reacts with $\text{MeSCH}_2\text{CH}_2\text{Cl}$ to give, together with other products, a small amount of $\text{CpFe}(\text{CO})\text{COCH}_2\text{CH}_2\text{SMe}$ (142, 143). Similar heterocyclic complexes have been obtained, also in low yields, by using $\text{ClCH}_2\text{CH}_2\text{NMe}_2$ and $2\text{-(ClCH}_2)_2\text{C}_3\text{H}_4\text{N}$ [but not $2\text{-(ClCH}_2\text{CH}_2)_2\text{C}_3\text{H}_7\text{NH}$] as the source of entering ligands (144).

Reactions of $\text{CpFe}(\text{CO})_2\text{Me}$ with PPh_3 in hydrocarbon solvents at reflux have afforded $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{COMe}$ and $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{Me}$ (219). The former decarbonylates to the latter on heating, indicating that the original reaction was a two-step process: insertion [Eq. (14)] followed by CO elimination [Eq. (15)]. Under comparable conditions, the ethyl dicarbonyl and PPh_3 furnish $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{COEt}$ and $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{H}$ [see Eq. (60)]. The hydride was shown to result from elimination of C_2H_4 by the ethyl monocarbonyl. The phenyl dicarbonyl also yields two products— $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{COPh}$ and $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{Ph}$ —upon treatment with

PPh_3 in benzene at reflux (188). However, $\text{CpFe}(\text{CO})_2\text{C}\equiv\text{CR}$ ($\text{R} = \text{Bu}$ or Ph) and PPh_3 afford only the respective monosubstitution products (102).

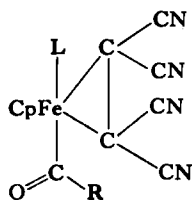
Photochemical reactions of $\text{CpFe}(\text{CO})_2\text{R}$ [$\text{R} = \text{Me}$ (227), Et (219), CH_2SiMe_3 (201), R_F (149), Ph (185–188), and various substituted Ph (187, 188, 190), *inter alia*] with L [$\text{L} = \text{PPh}_3$, $\text{P}(\text{OPh})_3$, and related P donor ligands] almost invariably yield $\text{CpFe}(\text{CO})\text{LR}$. Oftentimes, especially when elevated temperatures are employed, $\text{CpFe}(\text{CO})\text{L}(\text{COR})$ is also produced (185, 186, 188) and is believed to arise through a competing thermal reaction. The observation that, under comparable conditions, the reaction (219)



proceeds faster than the photochemical decarbonylation of $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{COEt}$ militates against the intermediacy of this propionyl in the former process. Like the propionyl complex, the analogous $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{COPh}$ (188) and $-\text{COMe}$ (219) [contrary to the original report (227)], can be decarbonylated by using ultraviolet light.

Carbon monoxide insertion reactions of $\text{CpFe}(\text{CO})\text{LR}$ are not common. The complex $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{Me}$ can be converted to the acetyl monocarbonyl with CO in refluxing petroleum ether ($\sim 100^\circ\text{C}$) (227). By contrast, ultraviolet light-promoted reaction between $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{R}$ ($\text{R} = \text{Ph}$ or $p\text{-C}_6\text{H}_4\text{F}$) and CO yields $\text{CpFe}(\text{CO})_2\text{R}$ (188).

Only $\text{CpFe}(\text{CO})[\text{P}(\text{OR})_3]\text{Me}$ have been obtained upon treatment of $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{Me}$ with various $\text{P}(\text{OR})_3$ in THF at reflux (219). However, the reaction of $\text{CpFe}(\text{CO})\text{LR}$ [$\text{L} = \text{PPh}_3$, $\text{R} = \text{Me}$, Et , and $n\text{-Pr}$; $\text{L} = \text{P}(n\text{-Bu})_3$, $\text{R} = \text{Me}$; $\text{L} = \text{P}(\text{OPh})_3$, $\text{R} = \text{Me}$] with the electrophile tetracyanoethylene did result in the formation of acyl complexes of proposed structure (XXVIII) (220).



(XXVIII)

The carbonyl $[\text{CpFe}(\text{CO})_2]_2$ has been successfully employed as a catalyst for hydroformylation of propylene (229) and for the reaction in Eq. (55) (221). Insertion of CO into $\text{Fe}-\text{C}$ bonds is thought to occur therein.

Apart from the foregoing cyclopentadienyl systems, few alkyliron carbonyl complexes have been studied. Treatment of $\text{Na}_2\text{Fe}(\text{CO})_4$ with $\text{R}_\text{F}\text{COCl}$ ($\text{R}_\text{F} = \text{C}_2\text{F}_5$ or C_3F_7) has afforded $(\text{R}_\text{F})_2\text{Fe}(\text{CO})_4$ (152), no doubt via the intermediacy of the corresponding diacyls. The tetracarbonylferrate(–II) ion, as well as $\text{HFe}(\text{CO})_4^-$ and polynuclear carbonylferrates, has been utilized in the synthesis of aldehydes from alkyl halides and of carboxylic esters from alkene oxides and alcohols (74, 222, 224). These reactions are considered to proceed through the initial formation of an iron alkyl, followed by CO insertion and cleavage of the $\text{Fe}-\text{COR}$ bond. Several ionic $(\text{Ph}_3\text{P})_2\text{N}[\text{RCOFe}(\text{CO})_4]$ ($\text{R} = \text{Me}$, Et , $n\text{-Bu}$, CH_2Ph , Ph , and $\text{CH}=\text{CH}_2$) have been isolated by treatment of $\text{Na}_2[\text{Fe}(\text{CO})_4]$ with RBr under CO followed by addition of $(\text{Ph}_3\text{P})_2\text{NCl}$ (215a). A significant recent observation is that the rate of reaction between $\text{Me}(\text{CH}_2)_8\text{Fe}(\text{CO})_4^-$ and PR_3 to give $\text{Me}(\text{CH}_2)_8\text{COFe}(\text{CO})_3\text{PR}_3^-$ depends markedly on the nature of the cation, $\text{Li}^+ > \text{Na}^+ \gg (\text{Ph}_3\text{P})_2\text{N}^+$, spanning a range of at least three orders of magnitude (70a). These results are consistent with a mechanism in which an ion pair is the kinetically reactive species.

Oxidative addition of MeI to *trans*- $\text{Fe}(\text{CO})_3(\text{PMe}_3)_2$ yields $\text{MeCOFe}(\text{CO})_2(\text{PMe}_3)_2\text{I}$, very likely by way of an ionic $\text{MeFe}(\text{CO})_3(\text{PMe}_3)_2^+\text{I}^-$ (200). The above acetyl undergoes decarbonylation to $\text{MeFe}(\text{CO})_2(\text{PMe}_3)_2\text{I}$, the reaction being reversible [Eq. (49)]. By contrast, $\text{MeFe}(\text{CO})_2(\text{PMe}_3)_2\text{I}$ is stable to excess PMe_3 on warming. Similar oxidative additions with CO insertion have been detected spectroscopically for *trans*- $\text{Fe}(\text{CO})_3(\text{PMe}_3)_2$ and EtX ($\text{X} = \text{Br}$ or I).

Complexes of formula $\text{RCOFe}(\text{CO})_3\text{NO}$ can be detected spectroscopically when $\text{NaFe}(\text{CO})_3\text{NO}$ is allowed to react with MeI , EtI , PhCH_2Cl , MeOCH_2Cl , or $\text{ClCH}_2\text{CO}_2\text{Et}$ (64). Inclusion of PPh_3 in these reaction mixtures furnishes $\text{RCOFe}(\text{CO})_2(\text{NO})\text{PPh}_3$, which are isolable. Two pathways are believed to operate:



2. Ruthenium

The reaction of $\text{CpRu}(\text{CO})_2\text{Me}$ with PR_3 ($\text{R} = \text{C}_6\text{H}_{11}$ or Ph) at 160–180° affords the expected $\text{CpRu}(\text{CO})(\text{PR}_3)\text{COMe}$ (101). The temperatures employed are suggestive of the lower reactivity of $\text{CpRu}(\text{CO})_2\text{R}$ than $\text{CpFe}(\text{CO})_2\text{R}$ in the insertion.

3. Osmium

Attempts at carbonylation with CO at high pressures or with PPh_3 of $\text{H}(\text{Me})\text{Os}(\text{CO})_4$ and $\text{Me}_2\text{Os}(\text{CO})_4$ have been unsuccessful (163). By contrast, the reaction of *cis*- $\text{Et}_2\text{Os}(\text{CO})_4$ with 100 atm of CO at 110° gives *cis*- $(\text{EtCO})_2\text{Os}(\text{CO})_4$ (163). An ionic acetyl, $(\text{MgBr})_2[(\text{MeCO})_2\text{Os}(\text{CO})_2\text{Br}_2] \cdot 5\text{THF}$, results from treatment of $\text{Os}(\text{CO})_4\text{Br}_2$ with MeMgBr (162). The mechanism of its formation is unknown.

E. Cobalt Triad

1. Cobalt

Alkyl- and acylcobalt tetracarbonyls were the subject of a comprehensive review by Heck (115). Since then (1966), they have been given some attention in review articles concerned primarily with catalysis (62, 117, 118). Because of an extensive coverage afforded the early developments, emphasis herein will be on the more recent findings.

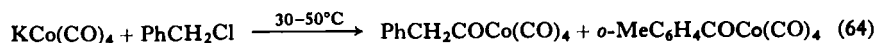
Complexes of the type $\text{RCo}(\text{CO})_4$, where R is a hydrocarbon fragment, have low stability (41, 131). They are readily carbonylated to the corresponding acyls, $\text{RCOCo}(\text{CO})_4$ (41, 167), and undergo reactions with phosphines or phosphites (L) to give $\text{RCOCo}(\text{CO})_3\text{L}$ (120, 121, 123, 217). The latter insertion is usually carried out by allowing $\text{NaCo}(\text{CO})_4$, RX, and L to react together in ether at $\sim 0^\circ\text{C}$. Many tricarbonyl acyls synthesized by this general procedure are reported by Heck. The dicarbonyl $\text{MeCOCo}(\text{CO})_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ is also obtainable (123).

An alternative route to $\text{RCOCo}(\text{CO})_3\text{L}$ employs a reaction of $\text{HCo}(\text{CO})_4$ with an olefin and L (111, 120, 122, 153), e.g. (120),



The importance of these and related processes in hydroformylation and other carbonylation reactions has been underscored by several reviewers (62, 115, 118) and will not be reiterated here.

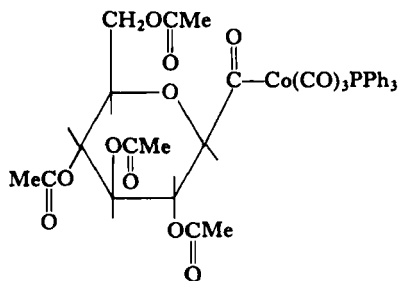
Among the later developments noteworthy is an isomerization in the reaction



which is promoted by $\text{HCo}(\text{CO})_4$, higher temperatures, and N_2 atmosphere (223). However, no rearrangement of the benzyl moiety was detected when $\text{NaCo}(\text{CO})_4$ reacts with PhCH_2Cl under CO at 20°C (177). The product is $\text{PhCH}_2\text{COCO}(\text{CO})_4$, in equilibrium with $\text{PhCH}_2\text{Co}(\text{CO})_4$, and rapidly

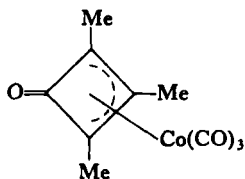
losing CO under Ar. Treatment of this equilibrium mixture with PPh_3 under CO affords $\text{PhCH}_2\text{COCO}(\text{CO})_3\text{PPh}_3$, which readily eliminates CO at 50°C . Both the acyl precursor and the alkyl product have idealized C_{3v} symmetry.

The carbohydrate 2,3,4,6-tetra-*O*-acetyl- α -D-glucopyranosyl bromide reacts with $\text{NaCo}(\text{CO})_4$ and PPh_3 under 10 atm of CO to yield the expected acetyl (XXIX) and the corresponding alkyl (210). The former decarbonylates readily on storage or chromatography. Retention of configuration at carbon accompanies CO elimination.



(XXIX)

The compound obtained from the reaction between trimethylcyclopropenyl bromide and $\text{Co}(\text{CO})_4^-$ has been shown spectroscopically to be (XXX) rather than a tricarbonyl acyl (146); the triphenyl analog (68) is believed to have a similar structure.



(XXX)

Carbonylation of $\text{MeCo}(\text{CO})_3\text{P}(p\text{-C}_6\text{H}_4\text{OMe})_3$ under mild conditions proceeds rapidly to the corresponding acetyl (110). The related $\text{MeCo}(\text{CO})_3\text{PPh}_3$ does not react with bulky PPh_3 ; however, on treatment with $\text{P}(\text{OMe})_3$ at 0°C it affords $\text{MeCOCO}(\text{CO})_2(\text{PPh}_3)\text{P}(\text{OMe})_3$, and with excess phosphite yields $\text{MeCOCO}(\text{CO})_2[\text{P}(\text{OMe})_3]_2$. The dicarbonyl $\text{MeCo}(\text{CO})_2\text{L}_2$ and L [$\text{L} = \text{P}(\text{OMe})_3$] at 75°C furnish $\text{MeCOCO}(\text{CO})\text{L}_3$; a

strictly analogous, but more facile reaction occurs when $L = P(OCH_2)_3Ct$. No insertion in $MeCo(CO)[P(OCH_2)_3Ct]_3$ could be effected with the phosphite at $100^\circ C$.

The perfluoroacetyltetracarbonyls $R_FCoCo(CO)_4$ ($R_F = CF_3$ and C_2F_5) exhibit higher stability toward the decarbonylation than their hydrocarbon counterparts. Temperatures of 30° – $60^\circ C$ are required for CO elimination (126, 130). However, when $R_F = C_3F_7$ or C_7F_{15} , the decarbonylation occurs in the course of synthesis from $Co(CO)_4^-$ and the acid anhydride at $\sim 25^\circ C$ (130). The corresponding tricarbonyls $R_FCoCo(CO)_3PPh_3$ ($R_F = CF_3$ and C_2F_5) lose CO more reluctantly (126, 130), and so do the less-fluorinated acyl tricarbonyls ($R = CF_2H$, CH_2F , and $m-C_6H_4F$) (164, 216). Unexpectedly, the decarbonylation occurs spontaneously during reaction between $NaCo(CO)_2(PPh_3)_2$ and $(CF_3CO)_2O$ at room temperature (128).

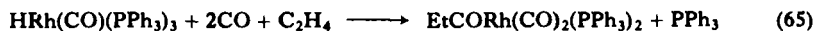
Interest has developed recently in cyclopentadienylcobalt carbonyl complexes. Oxidative addition of RI ($R = Me$ or Et) to $CpCo(CO)L$ ($L = PPh_3$, PMe_2Ph , or $PMePh_2$) yields initially $CpCo(CO)RL^+I^-$, which then undergoes rapid CO insertion to $CpCoL(COR)I$. The slow step has been studied kinetically (148). Compounds of the type $CpCo(CO)(R_F)I$ afford ionic substitution products when treated with chelating diphosphines (106).

Because of structural similarities to the vitamin B_{12} coenzyme, cobalt(III) complexes of the type $RCo(L_4)$ or $RCo(L_2)_2$ [$L_4 = \text{bis}(\text{salicylaldehyde})\text{-ethylenediimine}$ and $L_2 = \text{dimethylglyoximate}$, *inter alia*] have been actively investigated (40, 76, 77, 125). Corresponding acyl complexes have been synthesized (40, 76). However, neither the CO insertion into the $Co-R$ linkage nor the decarbonylation of the $Co-COR$ moiety has been achieved (77, 125). A probable reason for this was presented in Section II.

2. Rhodium

Carbon monoxide insertion and decarbonylation reactions of rhodium complexes have been studied mainly in the context of investigations concerned with catalysis.

Rhodium(I) alkyls and acyls are generally extremely labile. For example, the propionyl formed by CO insertion in the reaction (241, 242)

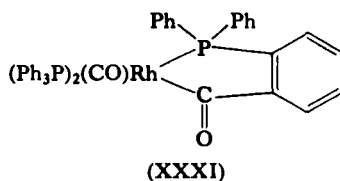


is stable only under an atmosphere of CO and C_2H_4 . Several equilibria involving hydrido, ethyl, and propionyl species are suggested to occur in solution. In the homogeneous hydroformylation of olefins with $HRh(CO)(PPh_3)_3$, the equilibrium (43)



is believed to prevail. The acyl then generates an aldehyde upon reaction with H_2 .

Treatment of $PhRh(PPh_3)_3$ with CO in solution was originally reported (137) to yield a complex thought to be $PhCORh(CO)(PPh_3)_2$. A reexamination (242) of this reaction by infrared spectroscopy suggests that $PhCORh(CO)_2(PPh_3)_2$ and $PhCORh(CO)_3PPh_3$ are produced instead. Passage of N_2 through a solution of the above acyls appears to effect decarbonylation to $PhRh(CO)(PPh_3)_2$. A high-pressure reaction with CO of $Rh(Ph_2PC_6H_4-o)(PPh_3)_2$ furnishes a complex of proposed structure (XXXI) (137).



Rhodium(I) complexes are effective reagents and/or catalysts for the decarbonylation of acyl halides and aldehydes (9-11, 34, 195, 230, 231, 236). The compound $Rh(PPh_3)_3Cl$, especially, has received considerable attention. The first step in such reactions involves oxidative addition to $Rh(I)$ of the organic molecule, exemplified by the following:



These five-coordinate acyls generally rapidly react further, although some have been isolated and characterized (10, 231). Rearrangement of the acyls to corresponding six-coordinate alkyls, followed by a reductive elimination of RCl or RH , completes the decarbonylation process. When R is an aryl group, or when mild conditions are employed, the intervening six-coordinate $RRh(CO)(PPh_3)_2Cl_2$ can be isolated (9, 10, 34, 195). An analogous aryl, $PhRh(CO)(Ph_2PC_6H_4-o)(PPh_3)Cl$, results when $Rh(Ph_2PC_6H_4-o)(PPh_3)_2$ reacts with $PhCOCl$ (137).

Treatment of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ with cyclopropanes (205) or cubanes (61) leads to an oxidative addition of the hydrocarbon to the Rh(I) species and is thought to involve CO insertion.

Hydroformylation of alkenes using $\text{Rh}(\text{CO})(\text{PR}_3)_2\text{X}$ has been discussed from a mechanistic viewpoint (89).

Alkyl complexes of Rh(III) manifest much higher stability than those of Rh(I). Carbon monoxide insertion into the Rh—Me bond of $\text{MeRh}(\text{CO})\text{—}[\text{P}(n\text{-Bu})_3]_2\text{IX}$ ($\text{X} = \text{Cl}$ and Br) (113) and $\text{MeRh}(\text{CO})(\text{PMe}_2\text{Ph})_2\text{Br}_2$ (84) has been effected at atmospheric pressures of CO. By contrast, carbonylation of $(\pi\text{-C}_3\text{H}_4\text{Me})\text{RhL}_2\text{Cl}_2$ ($\text{L} = \text{PPh}_3$ or AsPh_3) did not furnish rhodium acyl complexes (234). However, intermediates formulated as $(\text{MeC}_3\text{H}_4\text{CO})\text{—RhL}_2\text{Cl}_2$ were detected spectroscopically.

At low temperatures (-50° to -60°C), Rh(III) complexes of the type $\text{RRh}(\text{PPh}_3)_2\text{Cl}_2$ ($\text{R} = \text{Et}$ and $\text{CH}=\text{CH}_2$) absorb CO to give $\text{RRh}(\text{CO})\text{—}(\text{PPh}_3)_2\text{Cl}_2$; higher temperatures promote formation of the stable acyls $\text{RCORh}(\text{PPh}_3)_2\text{Cl}_2$ (10). However, when $\text{R} = \text{C}_2\text{F}_4\text{H}$, the reaction stops at the alkylcarbonyl stage. The equilibrium constant K for the reaction



increases in the order: $\text{R} = \text{Ph} < \text{Me} < \text{Et}$, presumably as a result of the relative Rh—C bond strengths.

Cyclopentadienylrhodium complexes of formula $\text{CpRh}(\text{CO})\text{L}$ ($\text{L} = \text{PPh}_3$ or PMe_2Ph) undergo oxidative addition reactions followed by CO insertion upon treatment with MeI , EtI , PhCH_2X , $\text{CH}_2=\text{CHCH}_2\text{X}$ ($\text{X} = \text{Cl}$, Br , or I), $\text{MeC}_3\text{H}_4\text{Cl}$, or $\text{BrCH}_2\text{CO}_2\text{Et}$ (RX) to yield $\text{CpRhL}(\text{COR})\text{X}$ (107, 196). The reverse of the insertion step has been effected for $\text{CpRh}(\text{PMe}_2\text{Ph})(\text{COMe})\text{Br}$ by using NaBPh_4 to precipitate cationic $\text{CpRh}(\text{CO})(\text{PMe}_2\text{Ph})\text{Me}^+$. The foregoing addition reactions, which are strictly analogous to those of the corresponding cobalt compounds, have been the subject of a kinetic study (106). Kinetic investigations have also been carried out (88, 233) on related oxidative addition–insertion transformations involving *trans*- $\text{Rh}(\text{CO})(\text{PR}_3)_2\text{X}$ and *trans*- $\text{Rh}(\text{CO})_2(\text{PPh}_3)\text{Cl}$ (87) (however, see footnote 2, Section III,A).

3. Iridium

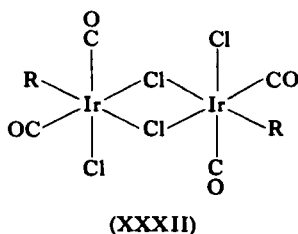
Iridium(I) complexes with metal–carbon σ -bonds are markedly more stable than those of Rh(I). In contrast to Rh(I), both $\text{EtCOIr}(\text{CO})_2(\text{PPh}_3)_2$

and $\text{EtCOIr}(\text{CO})(\text{PPh}_3)_2$ can be isolated (242). They result from the reaction of the hydride $\text{HIr}(\text{CO})_2(\text{PPh}_3)_2$ with $\text{C}_2\text{H}_4\text{—CO}$ and C_2H_4 alone, respectively, under pressure. There is infrared spectroscopic evidence for the decarbonylation of the former acyl to $\text{EtIr}(\text{CO})_2(\text{PPh}_3)_2$. The latter acyl equilibrates with the last-mentioned alkyl in solution. Reaction between $\text{PhIr}(\text{CO})(\text{PPh}_3)_2$ and CO affords $\text{PhCOIr}(\text{CO})_2(\text{PPh}_3)_2$, which can be isolated. Extrusion of the acyl CO from the benzoyl complex in solution occurs readily upon passage of N_2 . The analogous acetyl has been made by the reaction involving $\text{Ir}(\text{CO})(\text{PPh}_3)_2\text{Cl}$, MeLi , and CO (242), or by the carbonylation of $\text{MeIr}(\text{CO})_2(\text{PPh}_3)_2$ (72), both under pressure.

π -Allyl complexes of Ir(I) of the type $(\pi\text{-C}_3\text{H}_5\text{RR}')\text{Ir}(\text{CO})(\text{PPh}_3)_2$ (R and $\text{R}' = \text{H}$, Me , and $i\text{-Pr}$) undergo facile carbonylation to $(\text{RR}'\text{C}_3\text{H}_5\text{CO})\text{-Ir}(\text{CO})_2(\text{PPh}_3)_2$ (42). The reverse can be effected by heating.

Like its $\text{Rh}(\text{I})$ counterpart, $\text{Ir}(\text{PPh}_3)_3\text{Cl}$ reacts with RCOCl ($\text{R} = \text{Me}$, Ph , and $p\text{-C}_6\text{H}_4\text{Me}$) to provide six-coordinate $\text{RIr}(\text{CO})(\text{PPh}_3)_2\text{Cl}_2$, which are, however, stable (159). These products no doubt result from rearrangement of the initially formed five-coordinate acyls. Similar Ir(III) alkyl compounds are accessible from *trans*- $\text{Ir}(\text{PPh}_3)_2(\text{N}_2)\text{Cl}$ and RCOCl . When $\text{R} = \text{Et}$, $(\text{CH}_2)_{10}\text{Me}$, Cpr , cyclobutyl, and CH=CH_2 , the intermediate acyl derivatives have been detected by infrared spectroscopy. However, with $\text{R} = \text{Me}$, Ph , and C_6F_5 , only the final products are observable. Stability of the five-coordinate acyls appears to be greatest when $\text{R} = \text{CH}_2\text{C}_6\text{H}_4\text{X}$ ($\text{X} = \text{H}$ or another substituent), permitting isolation and a kinetic study of the acyl-to-alkyl rearrangement (160) (Section IV).

The complex $[\text{Ir}(\text{CO})(\text{C}_8\text{H}_{14})_2\text{Cl}]_2$ ($\text{C}_8\text{H}_{14} = \text{cyclooctene}$) also oxidatively adds RCOCl to yield $\text{R}_2\text{Ir}_2(\text{CO})_4\text{Cl}_4$ (XXXII; $\text{R} = \text{Me}$, Et , $i\text{-Pr}$, or Ph) (7, 215). Evidence suggests a two-step reaction, the second step



involving a migration of R from the initially formed acyl moiety. When $\text{R} = \text{Me}$ or Et , (XXXII) reacts with tertiary phosphines and arsines (L) first to furnish $\text{RIr}(\text{CO})_2\text{LCl}_2$, and then $[\text{RCOIr}(\text{CO})\text{LCl}_2]_2$ or $\text{RCOIr}(\text{CO})\text{L}_2\text{Cl}_2$, depending on the nature of L . The formation of $\text{RCOIr}(\text{CO})\text{-}$

L_2Cl_2 from $RIr(CO)_2LCl_2$ and L has been the subject of kinetic and stereochemical studies (92, 94), discussed in Sections III and V.

Unlike their $Rh(III)$ analogs, $RIr(CO)(PR_3)_2X_2$ do not react readily with CO. Accordingly, neither $MeIr(CO)[P(n-Bu)_3]_2ICl$ (113) nor $MeIr(CO)-(PMePh_2)_2BrCl$ (71) is carbonylated at atmospheric pressures. Carbon monoxide insertion does occur with $MeIr(CO)(PPh_3)_2Cl_2$ under 20 psi of CO in CH_2Cl_2 -MeOH, but not in benzene (159). The analogous dibromo complex does not insert even under the above conditions of higher pressure.

The decarbonylation of six-coordinate $Ir(III)$ acyls is generally not a facile process. It has been effected by heating to $\sim 200^\circ C$ the following complexes: $PhCOIr(CO)(PMePh_2)_2Cl_2$ (159), $MeCOIr(CO)(PEt_2Ph)_2Br_2$ (63), $PhCOIr(CO)(PMe_2Ph)_2Cl_2$ (85); $MeCOIr(CO)(PPh_3)_2Cl_2$, and $Me(CH_2)_9COIr(CO)(PPh_3)_2Cl_2$ (33a). However, the complexes $RCOIr(CO)(PPh_3)_2Cl_2$ ($R = Ph$, $p-C_6H_4OEt$, $p-C_6H_4NO_2$, $3,4-C_6H_3Cl_2$, and $2-C_4H_3S$) liberate CO at $45^\circ C$ (33a).

Oxidative addition of RX to square-planar $Ir(CO)L_2X$ or to $CpIr(CO)L$ ($L = PR_3$ or AsR_3) invariably affords $RIr(CO)L_2X_2$ (71, 85, 86) and $CpIr(CO)LR^+X^-$ (106, 198), respectively. Unlike some of their rhodium analogs, these complexes do not rearrange to the acyls.

F. Nickel Triad

1. Nickel

Carbonylation of $CpNiC_8H_{13}$ ($C_8H_{13} = \sigma, \pi$ -cyclooctenyl) under pressure has afforded an unisolable acyl, $CpNi(COC_8H_{13})$, characterized only by mass spectrometry (19). Treatment of $CpNi(PR_3)Me$ ($R = n-Bu$ or Ph) (206) or $CpNi(PPh_3)Ph$ (247) with CO, also under pressure, produced no evidence of carbon monoxide insertion.

Carbon monoxide insertion into $Ni-C$ bonds has been postulated in carbonylation reactions involving $(\pi-C_3H_5NiX)_2$ ($X = Cl, Br, \text{ or } I$) (112, 123a).

Oxidative addition of C_6F_5COCl to $Ni(PPh_3)_2(C_2H_4)$ yields *trans*- $Ni(PPh_3)_2(C_6F_5)Cl$ (5), presumably via the corresponding aryl.

2. Palladium

Square-planar $Pd(II)$ complexes of the type *trans*- $Pd(PR_2R')_2(Me)X$ ($X = Cl$ or Br , $R = R' = Et$; $X = Cl$, $R = Me$, $R' = Ph$) undergo facile reaction with CO at 1-3 atm and room temperature to yield the corresponding *trans*- $Pd(PR_2R')_2(COMe)X$ (38, 39, 66). However, $Me_2Pd-(PEt_3)_2$ and CO afford unstable, uncharacterized products (39).

Palladium(0)- and Pd(II)-catalyzed carbonylation reactions have been the subject of several recent articles (32, 116, 119, 124, 173, 228, 232). In one case, the attending CO insertion into a Pd—C bond was shown to proceed with retention of configuration at carbon (131a, 218).

The reaction between $\text{Pd}(\text{PMePh}_2)_4$ and $n\text{-C}_3\text{F}_7\text{COCl}$ or $\text{C}_6\text{F}_5\text{COCl}$ yields, respectively, *trans*- $\text{Pd}(\text{PMePh}_2)_2(\text{COC}_3\text{F}_7)\text{Cl}$ and *trans*- $\text{Pd}(\text{PMePh}_2)_2(\text{C}_6\text{F}_5)\text{Cl}$ (175). The latter compound presumably arises through spontaneous decarbonylation of *trans*- $\text{Pd}(\text{PMePh}_2)(\text{COC}_6\text{F}_5)\text{Cl}$.

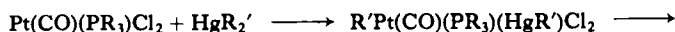
3. Platinum

Four-coordinate Pt(II) alkyls are not carbonylated as readily as their Pd(II) analogs. This is consistent with a lesser tendency of Pt(II) than of Pd(II) to expand its coordination number to 5. Thus, the reaction of *trans*- $\text{Pt}(\text{PEt}_3)_2(\text{Me})\text{X}$ (X = Cl or Br) with CO to give *trans*- $\text{Pt}(\text{PEt}_3)_2(\text{COMe})\text{X}$ requires a pressure of 80 atm and a temperature of 90°C (38, 39). Similar high-pressure carbonylations have been effected with *cis*- $\text{Pt}(\text{PEt}_3)_2(\text{Me})\text{Cl}$, *trans*- $\text{Pt}(\text{PEt}_3)_2(\text{Et})\text{I}$, *cis*- and *trans*- $\text{Pt}(\text{PEt}_3)_2(\text{Ph})\text{Cl}$, *trans*- $\text{Pt}(\text{PEt}_3)_2(\text{Ph})\text{I}$ (39), and *trans*- $\text{Pt}(\text{PMe}_2\text{Ph})_2(\text{Me})\text{Cl}$ (66). Only one Pt—Me bond participates in the CO insertion reaction of $\text{Me}_2\text{Pt}(\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2)$. By contrast, *cis*- $\text{Pt}(\text{PR}_3)_2\text{Me}_2$ (R = Et or Ph) loses its Me groups in the carbonylation. No CO insertion is observed, even at 120°C and under pressure, with *trans*- $\text{Pt}(\text{PPh}_3)_2(\text{Me})\text{I}$ (39). However, $\text{MeOC}_{10}\text{H}_{12}\text{Pt}(\text{PPh}_3)_2\text{Cl}$, where $\text{C}_{10}\text{H}_{12}\text{OMe}$ is 9-methoxytricyclo[5,2,1,0^{2,6}]dec-4-en-8-yl, reacts with CO under ambient conditions to yield stable acyl $\text{MeOC}_{10}\text{H}_{12}\text{COPt}(\text{PPh}_3)_2\text{Cl}$ (57a).

The dinuclear, Cl-bridged $[(\text{C}_8\text{H}_{17})\text{Pt}(\text{CO})\text{Cl}]_2$ reacts with excess PPh_3 to yield $(\text{C}_8\text{H}_{17}\text{CO})\text{Pt}(\text{PPh}_3)_2\text{Cl}$ (165, 240). A similar reaction is effected by $\text{P}(n\text{-Bu})_3$. The related mononuclear $\text{EtPt}(\text{CO})(\text{AsPh}_3)\text{Cl}$ reacts with AsPh_3 to afford $\text{EtCOPt}(\text{AsPh}_3)_2\text{Cl}$; this reaction was the subject of a kinetic study (93), mentioned earlier (Section III).

The cationic $(\pi\text{-C}_3\text{H}_3\text{R}_2)\text{Pt}(\text{PPh}_3)_2^+\text{Cl}^-$ (R = H) is converted to $(\text{MeCH}=\text{CHCO})\text{Pt}(\text{PPh}_3)_2\text{Cl}$ upon treatment with CO at 20°C (235). However, when R = Me, $(\text{Me}_2\text{C}=\text{CHCH}_2\text{CO})\text{Pt}(\text{PPh}_3)_2\text{Cl}$, with the C=C possibly coordinated to the metal, becomes the product.

Square-planar complexes $\text{Pt}(\text{CO})(\text{PR}_3)_2\text{Cl}_2$ (R = Ph or Bu) are transformed to the dinuclear $[\text{R}'\text{COPt}(\text{PR}_3)_2\text{Cl}]_2$ by the action of HgR'_2 (R' = Me or Ph) under mild conditions (82). These reactions are thought to proceed through the oxidative addition to Pt(II) of HgR'_2 , migration of R' onto CO, and elimination of $\text{R}'\text{HgCl}$.



Extrusion of CO from platinum acyl complexes of formula $\text{RCOPt}(\text{PR}'_3)_2\text{X}$ requires high temperatures. Decarbonylation has been effected when $\text{X} = \text{Cl}$, $\text{R} = \text{Me}$, and $\text{R}' = \text{Ph}$ ($210^\circ\text{--}220^\circ\text{C}$) (73); $\text{X} = \text{I}$, $\text{R} = \text{Me}$, and $\text{R}' = \text{Et}$ (140°C) (39); $\text{X} = \text{Cl}$ and $\text{R} = \text{R}' = \text{Ph}$ (210°C) (12); and $\text{X} = \text{Cl}$, $\text{R} = \text{C}_6\text{F}_5$, and $\text{R}' = \text{Ph}$ (188°C) (176). Several other Pt(II) acyls yield intractable decomposition products on heating (39). No successful carbon monoxide extrusion to give the corresponding alkyl complex has been reported for Pt(IV) . Generally, reductive elimination reactions leading to Pt(II) compounds occur instead (211–213).

G. Copper Triad

Carbon monoxide insertion reactions into Cu—C , Ag—C , or Au—C bonds are not known.

ACKNOWLEDGMENTS

The author is indebted to Dr. J. J. Alexander, Dr. J. P. Bibler, Dr. P. Reich-Rohrwig, and Dr. S. R. Su, his former graduate students and postdoctoral fellows, for their stimulating association with him and for their research contributions in this area of organometallic chemistry. Support of the research concerned with insertion reactions in the author's laboratories has been generously provided by the National Science Foundation.

REFERENCES

1. Alexander, J. J., and Wojcicki, A., *J. Organometal. Chem.* **15**, P23 (1968).
2. Alexander, J. J., and Wojcicki, A., *Inorg. Chim. Acta* **5**, 655 (1971).
- 2a. Alexander, J. J., and Wojcicki, A., *Inorg. Chem.* in press.
3. Angelici, R. J., *Organometal. Chem. Rev.* **3**, 173 (1968).
4. Anisimov, K. N., Kolobova, N. E., and Ioganson, A. A., *Izv. Akad. Nauk SSSR, Ser. Khim.* 749 (1969).
5. Ashley-Smith, J., Green, M., and Stone, F. G. A., *J. Chem. Soc., A* 3019 (1969).
6. Astakhova, I. S., Johannsson, A. A., Semion, V. A., Struchkov, Yu. T., Anisimov, K. N., and Kolobova, N. E., *Chem. Commun.* 488 (1969).
7. Bailey, N. A., Jones, C. J., Shaw, B. L., and Singleton, E., *Chem. Commun.* 1051 (1967).
8. Bainbridge, A., Craig, P. J., and Green, M., *J. Chem. Soc., A* 2715 (1968).
9. Baird, M. C., Lawson, D. N., Mague, J. T., Osborn, J. A., and Wilkinson, G., *Chem. Commun.* 129 (1966).
10. Baird, M. C., Mague, J. T., Osborn, J. A., and Wilkinson, G., *J. Chem. Soc., A* 1347 (1967).
11. Baird, M. C., Nyman, C. J., and Wilkinson, G., *J. Chem. Soc., A* 348 (1968).
12. Baird, M. C., and Wilkinson, G., *J. Chem. Soc., A* 865 (1967).
13. Bannister, W. D., Booth, B. L., Green, M., and Haszeldine, R. N., *J. Chem. Soc., A* 698 (1969).

14. Bannister, W. D., Booth, B. L., Haszeldine, R. N., and Loader, P. L., *J. Chem. Soc., A* 930 (1971).
15. Bannister, W. D., Green, M., and Haszeldine, R. N., *Chem. Commun.* 54 (1965).
16. Bannister, W. D., Green, M., and Haszeldine, R. N., *J. Chem. Soc., A* 194 (1966).
17. Barnett, K. W., Ph.D. Thesis, Univ. of Wisconsin (1967).
18. Barnett, K. W., *Inorg. Chem.* **8**, 2009 (1969).
19. Barnett, K. W., *J. Organometal. Chem.* **21**, 477 (1970).
- 19a. Barnett, K. W., Pollman, T. G., and Solomon, T. W., *J. Organometal. Chem.* **36**, C23 (1972).
- 19b. Barnett, K. W., Beach, D. L., and Pollmann, T. G., *Inorg. Nucl. Chem. Lett.* in press.
20. Barnett, K. W., and Treichel, P. M., *Inorg. Chem.* **6**, 294 (1967).
21. Basolo, F., and Pearson, R. G., "Mechanisms of Inorganic Reactions," pp. 578–609. Wiley, New York, 1967.
22. Beck, W., Hieber, W., and Tengler, H., *Chem. Ber.* **94**, 862 (1961).
23. Benaim, J., Mérour, J.-Y., and Roustan, J.-L., *Tetrahedron Lett.* 983 (1971).
24. Bennett, M. A., Robertson, G. B., Watt, R., and Whimp, P. O., *Chem. Commun.* 752 (1971).
25. Bennett, M. A., and Watt, R., *Chem. Commun.* 95 (1971).
26. Berger, M. N., Boocock, G., and Haward, R. N., *Advan. Catal.* **19**, 211 (1969).
27. Berry, A., and Brown, T. L., *J. Organometal. Chem.* **33**, C67 (1971).
28. Bibler, J. P., and Wojcicki, A., *Inorg. Chem.* **5**, 889 (1966).
29. Bird, C. W., *Chem. Rev.* **62**, 283 (1962); quoting unpublished results of T. H. Coffield and co-workers.
30. Bird, C. W., "Transition Metal Intermediates in Organic Synthesis." Academic Press, New York, 1967.
31. Bird, C. W., "Transition Metal Intermediates in Organic Synthesis," Chapter 6. Academic Press, New York, 1967.
32. Bittler, K., v. Kutepow, N., Neubauer, D., and Reis, H., *Angew. Chem., Int. Ed. Engl.* **7**, 329 (1968).
33. Blackmore, T., Bruce, M. I., Davidson, P. J., Iqbal, M. Z., and Stone, F. G. A., *J. Chem. Soc., A* 3153 (1970).
- 33a. Blum, J., Kraus, S., and Pickholtz, Y., *J. Organometal. Chem.* **33**, 227 (1971).
34. Blum, J., Oppenheimer, E., and Bergmann, E. D., *J. Amer. Chem. Soc.* **89**, 2338 (1967).
35. Booth, B. L., Green, M., Haszeldine, R. N., and Woffenden, N. P., *J. Chem. Soc., A* 920 (1969).
36. Booth, B. L., and Hargreaves, R. G., *J. Chem. Soc., A* 308 (1970).
37. Booth, B. L., Haszeldine, R. N., and Woffenden, N. P., *J. Chem. Soc., A* 1979 (1970).
38. Booth, G., and Chatt, J., *Proc. Chem. Soc.* 67 (1961).
39. Booth, G., and Chatt, J., *J. Chem. Soc., A* 634 (1966).
40. Booth, J., Craig, P. J., Dobbs, B., Pratt, J. M., Randall, G. L. P., and Williams, A. G., *J. Chem. Soc., A* 1964 (1971).
41. Breslow, D. S., and Heck, R. F., *Chem. Ind. (London)* 467 (1960).
42. Brown, C. K., Mowat, W., Yagupsky, G., and Wilkinson, G., *J. Chem. Soc., A* 850 (1971).
43. Brown, C. K., and Wilkinson, G., *J. Chem. Soc., A* 2753 (1970).
44. Bruce, M. I., Iqbal, M. Z., and Stone, F. G. A., *J. Organometal. Chem.* **20**, 161 (1969).
45. Brunner, H., Schindler, H.-D., Schmidt, E., and Vogel, M., *J. Organometal. Chem.* **24**, 515 (1970).
46. Brunner, H., and Schmidt, E., *Angew. Chem.* **81**, 570 (1969).
47. Burt, R., Cooke, M., and Green, M., *J. Chem. Soc., A* 2981 (1970).
48. Butler, I. S., Basolo, F., and Pearson, R. G., *Inorg. Chem.* **6**, 2074 (1967).

49. Calderazzo, F., in "Organic Syntheses via Metal Carbonyls" (I. Wender and P. Pino, eds.), pp. 245–251. Wiley (Interscience), New York, 1968.
50. Calderazzo, F., and Cotton, F. A., *Inorg. Chem.* **1**, 30 (1962).
51. Calderazzo, F., and Cotton, F. A., *Abstr. Int. Conf. Coordination Chem., Stockholm*, 1962, Paper 6H7.
52. Calderazzo, F., and Cotton, F. A., *Chim. Ind. (Milan)* **46**, 1165 (1964).
53. Calderazzo, F., and Noack, K., *J. Organometal. Chem.* **4**, 250 (1965).
54. Calderazzo, F., and Noack, K., *Coordination Chem. Rev.* **1**, 118 (1966).
55. Calderazzo, F., Noack, K., and Schaerer, U., *J. Organometal. Chem.* **6**, 265 (1966).
56. Capron-Cotigny, G., and Poilblanc, R., *C.R. Acad. Sci.* **263**, 885 (1966).
57. Carrick, A., and Glockling, F., *J. Chem. Soc., A* 913 (1968).
- 57a. Carturan, G., Graziani, M., and Belluco, U., *J. Chem. Soc., A* 2509 (1971).
58. Casey, C. P., *Chem. Commun.* 1220 (1970).
59. Casey, C. P., and Anderson, R. L., *J. Amer. Chem. Soc.* **93**, 3554 (1971).
60. Casey, C. P., and Bunnell, C. A., *J. Amer. Chem. Soc.* **93**, 4077 (1971).
61. Cassar, L., Eaton, P. E., and Halpern, J., *J. Amer. Chem. Soc.* **92**, 3515 (1970).
62. Chalk, A. J., and Harrod, J. F., *Advan. Organometal. Chem.* **6**, 119 (1968).
63. Chatt, J., Johnson, N. P., and Shaw, B. L., *J. Chem. Soc., A* 604 (1967).
64. Chaudhari, F. M., Knox, G. R., and Pauson, P. L., *J. Chem. Soc., C* 2255 (1967).
65. Churchill, M. R., and Fennessey, J. P., *Inorg. Chem.* **7**, 953 (1968).
66. Clark, H. C., and Puddephatt, R. J., *Inorg. Chem.* **9**, 2670 (1970).
67. Clark, H. C., and Puddephatt, R. J., *Inorg. Chem.* **10**, 18 (1971).
68. Coffey, C. E., *J. Amer. Chem. Soc.* **84**, 118 (1962).
69. Coffield, T. H., Kozikowski, J., and Closson, R. D., *J. Org. Chem.* **22**, 598 (1957).
70. Coffield, T. H., Kozikowski, J., and Closson, R. D., *Chem. Soc., Spec. Publ.* **13**, 126 (1959).
- 70a. Collman, J. P., Cawse, J. N., and Brauman, J. I., *J. Amer. Chem. Soc.* **94**, 5905 (1972).
71. Collman, J. P., and Sears, C. T., Jr., *Inorg. Chem.* **7**, 27 (1968).
72. Collman, J. P., Vastine, F. D., and Roper, W. R., *J. Amer. Chem. Soc.* **90**, 2282 (1968).
73. Cook, C. D., and Jauhal, G. S., *Can. J. Chem.* **45**, 301 (1967).
74. Cooke, M. P., Jr., *J. Amer. Chem. Soc.* **92**, 6080 (1970).
75. Cossee, P., in "Advances in the Chemistry of Coordination Compounds" (S. Kirschner, ed.), pp. 241–250. Macmillan, New York, 1961.
76. Costa, G., and Mestroni, G., *Tetrahedron Lett.* 1783 (1967).
77. Costa, G., Mestroni, G., and Pellizer, G., *J. Organometal. Chem.* **15**, 187 (1968).
78. Cotton, F. A., and Lukehart, C. M., *J. Amer. Chem. Soc.* **93**, 2672 (1971).
79. Craig, P. J., and Green, M., *Chem. Commun.* 1246 (1967).
80. Craig, P. J., and Green, M., *J. Chem. Soc., A* 1978 (1968).
81. Craig, P. J., and Green, M., *J. Chem. Soc., A* 157 (1969).
82. Cross, R. J., and Wardle, R., *J. Chem. Soc., A* 840 (1970).
83. Davis, J. W., and Kraihanzel, C. S., *Abstr. 162nd Nat. Meet., Amer. Chem. Soc., Washington*, 1971, INOR-172.
84. Deeming, A. J., and Shaw, B. L., *J. Chem. Soc., A* 597 (1969).
85. Deeming, A. J., and Shaw, B. L., *J. Chem. Soc., A* 1128 (1969).
86. Deeming, A. J., and Shaw, B. L., *J. Chem. Soc., A* 1562 (1969).
87. Deganello, G., Uguagliati, P., Crociani, B., and Belluco, U., *J. Chem. Soc., A* 2726 (1969).
88. Douek, I. C., and Wilkinson, G., *J. Chem. Soc., A* 2604 (1969).
89. Evans, D., Osborn, J. A., and Wilkinson, G., *J. Chem. Soc., A* 3133 (1968).
- 89a. Fachinetti, G., and Floriani, C., *Chem. Commun.* 654 (1972).
90. Fischer, E. O., and Maasböl, A., *Angew. Chem. Int. Ed. Engl.* **3**, 580 (1964).
- 90a. Floriani, C., and Fachinetti, G., *Chem. Commun.* 790 (1972).

91. Fong, C. W., and Kitching, W., *J. Organometal. Chem.* **22**, 95 (1970).
92. Glyde, R. W., and Mawby, R. J., *Inorg. Chim. Acta* **4**, 331 (1970).
93. Glyde, R. W., and Mawby, R. J., *Inorg. Chem.* **10**, 854 (1971).
94. Glyde, R. W., and Mawby, R. J., *Inorg. Chim. Acta* **5**, 317 (1971).
95. Green, M., and Hancock, R. I., *Chem. Commun.* 572 (1966).
96. Green, M., and Hancock, R. I., *J. Chem. Soc., A* 109 (1968).
97. Green, M., Hancock, R. I., and Wood, D. C., *J. Chem. Soc., A* 2718 (1968).
98. Green, M., and Westlake, D. J., *J. Chem. Soc., A* 367 (1971).
99. Green, M., and Wood, D. C., *J. Amer. Chem. Soc.* **88**, 4106 (1966).
100. Green, M. L. H., and Hurley, C. R., *J. Organometal. Chem.* **10**, 188 (1967).
101. Green, M. L. H., Mitchard, L. C., and Swanwick, M. G., *J. Chem. Soc., A* 794 (1971).
102. Green, M. L. H., and Mole, T., *J. Organometal. Chem.* **12**, 404 (1968).
103. Green, M. L. H., and Smith, M. J., *J. Chem. Soc., A* 3220 (1971).
104. Haines, L. I. B., and Poë, A. J., *J. Chem. Soc., A* 2826 (1969), and references therein.
105. Hanna, J. A., M.S. Thesis, Ohio State Univ. (1969).
106. Hart-Davis, A. J., and Graham, W. A. G., *Inorg. Chem.* **9**, 2658 (1970).
107. Hart-Davis, A. J., and Graham, W. A. G., *Inorg. Chem.* **10**, 1653 (1971).
108. Hart-Davis, A. J., and Mawby, R. J., *J. Chem. Soc., A* 2403 (1969).
109. Heck, R. F., *J. Amer. Chem. Soc.* **85**, 651 (1963).
110. Heck, R. F., *J. Amer. Chem. Soc.* **85**, 1220 (1963).
111. Heck, R. F., *J. Amer. Chem. Soc.* **85**, 1460 (1963).
112. Heck, R. F., *J. Amer. Chem. Soc.* **85**, 2013 (1963).
113. Heck, R. F., *J. Amer. Chem. Soc.* **86**, 2796 (1964).
114. Heck, R. F., *Amer. Chem. Soc., Spec. Publ.* **49**, 181 (1965).
115. Heck, R. F., *Advan. Organometal. Chem.* **4**, 243 (1966).
116. Heck, R. F., *J. Amer. Chem. Soc.* **90**, 5546 (1968).
117. Heck, R. F., in "Organic Syntheses via Metal Carbonyls" (I. Wender and P. Pino, eds.), pp. 373-403. Wiley (Interscience), New York, 1968.
118. Heck, R. F., *Accounts Chem. Res.* **2**, 10 (1969).
119. Heck, R. F., *Fortschr. Chem. Forsch.* **16**, 221 (1971).
120. Heck, R. F., and Breslow, D. S., *J. Amer. Chem. Soc.* **82**, 4438 (1960).
121. Heck, R. F., and Breslow, D. S., *J. Amer. Chem. Soc.* **83**, 1097 (1961).
122. Heck, R. F., and Breslow, D. S., *J. Amer. Chem. Soc.* **83**, 4023 (1961).
123. Heck, R. F., and Breslow, D. S., *J. Amer. Chem. Soc.* **84**, 2499 (1962).
- 123a. Heimbach, P., Jolly, P. W., and Wilke, G., *Advan. Organometal. Chem.* **8**, 29 (1970).
124. Henry, P. M., *Tetrahedron Lett.* 2285 (1968).
125. Herlinger, A. W., and Brown, T. L., *J. Amer. Chem. Soc.* **93**, 1790 (1971).
126. Hieber, W., Beck, W., and Lindner, E., *Z. Naturforsch. B* **16**, 229 (1961).
127. Hieber, W., Braun, G., and Beck, W., *Chem. Ber.* **93**, 901 (1960).
128. Hieber, W., and Duchatsch, H., *Chem. Ber.* **98**, 2933 (1965).
129. Hieber, W., Höfler, M., and Muschi, J., *Chem. Ber.* **98**, 311 (1965).
130. Hieber, W., and Lindner, E., *Chem. Ber.* **95**, 2042 (1962).
131. Hieber, W., Vohler, O., and Braun, G., *Z. Naturforsch. B* **13**, 192 (1958).
- 131a. Hines, L. F., and Stille, J. K., *J. Amer. Chem. Soc.* **94**, 485 (1972).
132. Hitch, R. R., Gondal, S. K., and Sears, C. T., Jr., *Chem. Commun.* 777 (1971).
133. Jolly, P. W., Bruce, M. I., and Stone, F. G. A., *J. Chem. Soc.* 5830 (1965).
134. Joshi, K. K., Pauson, P. L., and Stubbs, W. H., *J. Organometal. Chem.* **1**, 51 (1963).

135. Kaesz, H. D., King, R. B., and Stone, F. G. A., *Z. Naturforsch. B* **15**, 763 (1960).
136. Keblyls, K. A., and Filbey, A. H., *J. Amer. Chem. Soc.* **82**, 4204 (1960).
137. Keim, W., *J. Organometal. Chem.* **19**, 161 (1969).
138. King, R. B., *J. Amer. Chem. Soc.* **85**, 1918 (1963).
139. King, R. B., *J. Amer. Chem. Soc.* **85**, 1922 (1963).
140. King, R. B., *J. Amer. Chem. Soc.* **90**, 1417 (1968).
141. King, R. B., and Bisnette, M. B., *J. Organometal. Chem.* **2**, 15 (1964).
142. King, R. B., and Bisnette, M. B., *J. Amer. Chem. Soc.* **86**, 1267 (1964).
143. King, R. B., and Bisnette, M. B., *Inorg. Chem.* **4**, 486 (1965).
144. King, R. B., and Bisnette, M. B., *Inorg. Chem.* **5**, 293 (1966).
145. King, R. B., and Efraty, A., *Inorg. Chim. Acta* **4**, 123 (1970).
146. King, R. B., and Efraty, A., *J. Organometal. Chem.* **24**, 241 (1970).
147. King, R. B., Houk, L. W., and Kapoor, P. N., *Inorg. Chem.* **8**, 1792 (1969).
148. King, R. B., Kapoor, R. N., and Houk, L. W., *J. Inorg. Nucl. Chem.* **31**, 2179 (1969).
149. King, R. B., Kapoor, R. N., and Pannell, K. H., *J. Organometal. Chem.* **20**, 187 (1969).
150. King, R. B., and Korenowski, T. F., *J. Organometal. Chem.* **17**, 95 (1969).
151. King, R. B., Pannell, K. H., Bennett, C. R., and Ishaq, M., *J. Organometal. Chem.* **19**, 327 (1969).
152. King, R. B., Stafford, S. L., Treichel, P. M., and Stone, F. G. A., *J. Amer. Chem. Soc.* **83**, 3604 (1961).
153. Kirch, L., and Orchin, M., *J. Amer. Chem. Soc.* **81**, 3597 (1959).
154. Kitching, W., and Fong, C. W., *Organometal. Chem. Rev., Sect. A* **5**, 281 (1970).
155. Koerner v. Gustorf, E., and Grevels, F.-W., *Fortschr. Chem. Forsch.* **13**, 366 (1969).
156. Kraihanzel, C. S., and Maples, P. K., *J. Amer. Chem. Soc.* **87**, 5267 (1965).
157. Kraihanzel, C. S., and Maples, P. K., *Inorg. Chem.* **7**, 1806 (1968).
158. Kraihanzel, C. S., and Maples, P. K., *J. Organometal. Chem.* **20**, 269 (1969).
- 158a. Kruck, T., Höfler, M., and Liebig, L., *Chem. Ber.* **105**, 1174 (1972).
159. Kubota, M., and Blake, D. M., *J. Amer. Chem. Soc.* **93**, 1368 (1971).
160. Kubota, M., Blake, D. M., and Smith, S. A., *Inorg. Chem.* **10**, 1430 (1971).
161. Lappert, M. F., and Prokai, B., *Advan. Organometal. Chem.* **5**, 225 (1967).
162. L'Eplattenier, F., *Inorg. Chem.* **8**, 965 (1969).
163. L'Eplattenier, F., and Pélichet, C., *Helv. Chim. Acta* **53**, 1091 (1970).
164. Lindner, E., Stich, H., Geibel, K., and Kranz, H., *Chem. Ber.* **104**, 1524 (1971).
165. Lodewijk, E., and Wright, D., *J. Chem. Soc., A* 119 (1968).
166. Maples, P. K., and Kraihanzel, C. S., *J. Amer. Chem. Soc.* **90**, 6645 (1968).
167. Marko, L., Bor, G., Almasy, G., and Szabo, P., *Brennst. Chem.* **44**, 184 (1963).
168. Mawby, R. J., Basolo, F., and Pearson, R. G., *J. Amer. Chem. Soc.* **86**, 3994 (1964).
169. Mawby, R. J., Basolo, F., and Pearson, R. G., *J. Amer. Chem. Soc.* **86**, 5043 (1964).
170. Mawby, R. J., Moris, D., Thorsteinson, E. M., and Basolo, F., *Inorg. Chem.* **5**, 27 (1966).
171. McClellan, W. R., *J. Amer. Chem. Soc.* **83**, 1598 (1961).
172. McCleverty, J. A., and Wilkinson, G., *J. Chem. Soc.* 4096 (1963).
173. Medema, D., van Helden, R., and Kohll, C. F., *Inorg. Chim. Acta* **3**, 255 (1969).
174. Morris, D. E., and Tinker, H. B., *Abstr. 162nd Nat. Meet., Amer. Chem. Soc., Washington, 1971*, INOR-173.
175. Mukhedkar, A. J., Green, M., and Stone, F. G. A., *J. Chem. Soc., A* 3023 (1969).
176. Mukhedkar, A. J., Green, M., and Stone, F. G. A., *J. Chem. Soc., A* 947 (1970).

177. Nagy-Magos, Z., Bor, G., and Marko, L., *J. Organometal. Chem.* **14**, 205 (1968).
178. Nesmeyanov, A. N., Anisimov, K. N., and Kolobova, N. E., *Izv. Akad. Nauk SSSR, Ser. Khim.* 1348 (1963).
179. Nesmeyanov, A. N., Anisimov, K. N., and Kolobova, N. E., *Izv. Akad. Nauk SSSR, Ser. Khim.* 1356 (1964).
180. Nesmeyanov, A. N., Anisimov, K. N., and Kolobova, N. E., *Izv. Akad. Nauk SSSR, Ser. Khim.* 2247 (1964).
181. Nesmeyanov, A. N., Anisimov, K. N., Kolobova, N. E., and Ioganson, A. A., *Dokl. Akad. Nauk SSSR* **175**, 358 (1967).
182. Nesmeyanov, A. N., Anisimov, K. N., Kolobova, N. E., and Ioganson, A. A., *Dokl. Akad. Nauk SSSR* **175**, 1293 (1967).
183. Nesmeyanov, A. N., Anisimov, K. N., Kolobova, N. E., and Ioganson, A. A., *Izv. Akad. Nauk SSSR, Ser. Khim.* 395 (1968).
184. Nesmeyanov, A. N., Anisimov, K. N., Kolobova, N. E., and Ioganson, A. A., *Izv. Akad. Nauk SSSR, Ser. Khim.* 1892 (1968).
185. Nesmeyanov, A. N., Chapovsky, Yu. A., Lokshin, B. V., Polovyanyuk, I. V., and Makarova, L. G., *Dokl. Akad. Nauk SSSR* **166**, 1125 (1966).
186. Nesmeyanov, A. N., Chapovsky, Yu. A., Polovyanyuk, I. V., and Makarova, L. G., *J. Organometal. Chem.* **7**, 329 (1967).
187. Nesmeyanov, A. N., Chapovsky, Yu. A., and Ustynyuk, Yu. A., *J. Organometal. Chem.* **9**, 345 (1967).
188. Nesmeyanov, A. N., Makarova, L. G., and Polovyanyuk, I. V., *J. Organometal. Chem.* **22**, 707 (1970).
189. Nesmeyanov, A. N., Makarova, L. G., and Ustynyuk, N. A., *J. Organometal. Chem.* **23**, 517 (1970).
190. Nesmeyanov, A. N., Polovyanyuk, I. V., Lokshin, B. V., Chapovsky, Yu. A., and Makarova, L. G., *Zh. Obshch. Khim.* **37**, 2015 (1967).
191. Noack, K., and Calderazzo, F., *J. Organometal. Chem.* **10**, 101 (1967).
192. Noack, K., Ruch, M., and Calderazzo, F., *Inorg. Chem.* **7**, 345 (1968).
193. Noack, K., Schaerer, U., and Calderazzo, F., *J. Organometal. Chem.* **8**, 517 (1967).
194. Ogilvie, J. F., *Chem. Commun.* 323 (1970).
195. Ohno, K., and Tsuji, J., *J. Amer. Chem. Soc.* **90**, 99 (1968).
196. Oliver, A. J., and Graham, W. A. G., *Inorg. Chem.* **9**, 243 (1970).
197. Oliver, A. J., and Graham, W. A. G., *Inorg. Chem.* **9**, 2578 (1970).
198. Oliver, A. J., and Graham, W. A. G., *Inorg. Chem.* **9**, 2653 (1970).
- 198a. Orchin, M., and Rupilius, W., *Catal. Rev.* **6**, 85 (1972).
199. Palagyi, J., and Marko, L., *J. Organometal. Chem.* **17**, 453 (1969).
200. Pańkowski, M., and Bigorgne, M., *J. Organometal. Chem.* **30**, 227 (1971).
201. Pannell, K. H., *J. Organometal. Chem.* **21**, P17 (1970).
202. Parshall, G. W., *J. Amer. Chem. Soc.* **87**, 2133 (1965).
203. Parshall, G. W., and Mrowca, J. J., *Advan. Organometal. Chem.* **7**, 157 (1968).
- 203a. Paulik, F. E., *Catal. Rev.* **6**, 49 (1972).
204. Poilblanc, R., and Gallay, J., *J. Organometal. Chem.* **27**, C53 (1971).
205. Powell, K. G., and McQuillin, F. J., *Chem. Commun.* 931 (1971).
206. Rausch, M. D., Chang, Y. F., and Gordon, H. B., *Inorg. Chem.* **8**, 1355 (1969).
207. Rausch, M. D., Criswell, T. R., and Ignatowicz, A. K., *J. Organometal. Chem.* **13**, 419 (1968).
208. Reich-Rohrwig, P., and Wojcicki, A., unpublished results (1971).
209. Rest, A. J., *J. Organometal. Chem.* **25**, C30 (1970).
210. Rosenthal, A., and Koch, H. J., *Tetrahedron Lett.* 871 (1967).
211. Ruddick, J. D., and Shaw, B. L., *J. Chem. Soc., A* 2801 (1969).

212. Ruddick, J. D., and Shaw, B. L., *J. Chem. Soc., A* 2964 (1969).
213. Ruddick, J. D., and Shaw, B. L., *J. Chem. Soc., A* 2969 (1969).
214. Schuster-Woldan, H. G., and Basolo, F., *J. Amer. Chem. Soc.* **88**, 1657 (1966).
215. Shaw, B. L., and Singleton, E., *J. Chem. Soc., A* 1683 (1967).
- 215a. Siegl, W. O., and Collman, J. P., *J. Amer. Chem. Soc.* **94**, 2516 (1972).
216. Steele, D. F., and Stephenson, T. A., *Inorg. Nucl. Chem. Lett.* **7**, 877 (1971).
217. Stewart, R. P., and Treichel, P. M., *J. Amer. Chem. Soc.* **92**, 2710 (1970).
218. Stille, J. K., and Hines, L. F., *J. Amer. Chem. Soc.* **92**, 1798 (1970).
219. Su, S. R., and Wojcicki, A., *J. Organometal. Chem.* **27**, 231 (1971).
220. Su, S. R., and Wojcicki, A., *J. Organometal. Chem.* **31**, C34 (1971).
221. Susuki, T., and Tsuji, J., *J. Org. Chem.* **35**, 2982 (1970).
222. Takegami, Y., Watanabe, Y., Masada, H., and Kanaya, I., *Bull. Chem. Soc. Jap.* **40**, 1456 (1967).
223. Takegami, Y., Watanabe, Y., Masada, H., and Yokokawa, C., *Bull. Chem. Soc. Jap.* **39**, 1499 (1966).
224. Takegami, Y., Watanabe, Y., Mitsudo, T., and Masada, H., *Bull. Chem. Soc. Jap.* **42**, 202 (1969).
225. Treichel, P. M., and Benedict, J. J., *J. Organometal. Chem.* **17**, P37 (1969).
226. Treichel, P. M., Pitcher, E., and Stone, F. G. A., *Inorg. Chem.* **1**, 511 (1962).
227. Treichel, P. M., Shubkin, R. L., Barnett, K. W., and Reichard, D., *Inorg. Chem.* **5**, 1177 (1966).
228. Tsuji, J., *Accounts Chem. Res.* **2**, 144 (1969).
229. Tsuji, J., and Mori, Y., *Bull. Chem. Soc. Jap.* **42**, 527 (1969).
230. Tsuji, J., and Ohno, K., *Tetrahedron Lett.* 4713 (1966).
231. Tsuji, J., and Ohno, K., *J. Amer. Chem. Soc.* **88**, 3452 (1966).
232. Tsuji, J., and Ohno, K., *J. Amer. Chem. Soc.* **90**, 94 (1968).
233. Uguagliati, P., Palazzi, A., Deganello, G., and Belluco, U., *Inorg. Chem.* **9**, 724 (1970).
234. Volger, H. C., and Vrieze, K., *J. Organometal. Chem.* **13**, 479 (1968).
235. Volger, H. C., and Vrieze, K., *J. Organometal. Chem.* **13**, 495 (1968).
236. Walborsky, H. M., and Allen, L. E., *J. Amer. Chem. Soc.* **93**, 5465 (1971).
237. Whitesides, G. M., and Boschetto, D. J., *J. Amer. Chem. Soc.* **91**, 4313 (1969).
238. Wilford, J. B., and Stone, F. G. A., *Inorg. Chem.* **4**, 93 (1965).
239. Wojcicki, A., *Accounts Chem. Res.* **4**, 344 (1971).
240. Wright, D., *Chem. Commun.* 197 (1966).
241. Yagupsky, G., Brown, C. K., and Wilkinson, G., *Chem. Commun.* 1244 (1969).
242. Yagupsky, G., Brown, C. K., and Wilkinson, G., *J. Chem. Soc., A* 1392 (1970).
243. Yagupsky, G., Mowat, W., Shortland, A., and Wilkinson, G., *Chem. Commun.* 1369 (1970).
244. Yamamoto, Y., and Hagihara, N., *Bull. Chem. Soc. Jap.* **39**, 1084 (1966).
245. Yamamoto, Y., and Yamazaki, H., *Bull. Chem. Soc. Jap.* **43**, 143 (1970).
246. Yamamoto, Y., and Yamazaki, H., *J. Organometal. Chem.* **24**, 717 (1970).
- 246a. Yamamoto, Y., and Yamazaki, H., *Inorg. Chem.* **11**, 211 (1972).
247. Yamazaki, H., Nishido, T., Matsumoto, Y., Sumida, S., and Hagihara, N., *J. Organometal. Chem.* **6**, 86 (1966).
248. Zakharkin, L. I., Kovredov, A. I., Kolobova, N. E., and Isaikina, T. A., *Izv. Akad. Nauk SSSR, Ser. Khim.* 497 (1970).
249. Zakharkin, L. I., and Orlova, L. V., *Izv. Akad. Nauk SSSR, Ser. Khim.* 2417 (1970).
250. Zakharkin, L. I., Orlova, L. V., Kovredov, A. I., Fedorov, L. A., and Lokshin, B. V., *J. Organometal. Chem.* **27**, 95 (1971).

This Page Intentionally Left Blank

Recent Advances in Organothallium Chemistry

ALEXANDER MCKILLOP

*School of Chemical Sciences
University of East Anglia
Norwich, England*

EDWARD C. TAYLOR

*Department of Chemistry
Princeton University
Princeton, New Jersey*

I. Introduction	147
II. Organothallium(I) Compounds	148
Cyclopentadienylthallium(I) and Related Compounds	149
III. Organothallium(III) Compounds	155
A. Preparation and Properties of R_3Tl Compounds	155
B. Preparation and Properties of R_2TlX Compounds	156
C. Preparation and Properties of $RTlX_2$ Compounds	160
References	202

I

INTRODUCTION

The discovery of thallium in 1861 did not, unlike the discovery of many elements, represent a milestone in the development of modern chemistry. The chemistry of thallium and its compounds has developed relatively slowly and, during the first half of this century, was largely unspectacular. Especially from the organic chemist's viewpoint, thallium has long been regarded as an obscure metal, organothallium chemistry as rather dull and predictable, and the utility of thallium compounds in organic chemistry as virtually nonexistent. These attitudes are now no longer tenable, largely as a result of the advances which have followed from the pioneering work of Menzies (33, 103), Gilman and Abbott (42), Glushkova and Kocheshkov (46), Criegee (27), and Kabbe (61). More than fifty specific synthetic organic transformations have now been described which involve the use of thallium reagents, and many proceed via the intermediacy of organothallium compounds. Parallel with these developments in the applications of thallium and its compounds to organic synthesis, there has been a rapid expansion

of interest in some of the more fundamental aspects of organothallium chemistry such as bonding, structure, mechanism, and spectroscopic properties.

Fortunately, this surge of interest in the chemistry of thallium during the last twenty years has been accompanied by a number of timely reviews of various aspects of the subject. Since 1967, five comprehensive reviews of organothallium chemistry have been published which adequately survey the preparation and properties of organothallium compounds (73, 78, 79, 111, 172); two short articles dealing with some of the applications of thallium compounds to organic synthesis have appeared recently (154, 155). The present review consists of a survey of the major trends in organothallium chemistry during the last twenty years, with particular emphasis on the applications of organothallium compounds to organic chemistry. Much of the review is therefore devoted to thallation and oxythallation, and to the utility of these processes in organic synthesis. Coverage has been restricted to organometallic compounds; the chemistry of derivatives of thallium with Group V and VI elements has been reviewed recently (79).

II

ORGANOTHALLIUM(I) COMPOUNDS

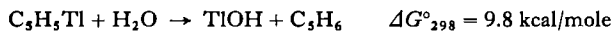
Organothallium(I) compounds in which the bonding is largely covalent have never been isolated. Treatment of thallium(I) halides with organolithium or Grignard reagents results in direct formation of either organothallium(III) derivatives or organic products, which have been presumed to arise via the intermediacy of initially formed, unstable organothallium(I) species. Thus, treatment of thallium(I) iodide with methyllithium in the presence of methyl iodide gives trimethylthallium (43, 44); the analogous reaction between phenyllithium and thallium(I) chloride gives triphenylthallium and thallium metal, even at -70°C (45). With the less nucleophilic Grignard reagents, this type of reaction generally gives either diorganothallium derivatives [but see (54a)] or organic products, the nature of which depends on the type and structure of the Grignard reagent, and, apparently, the solvent. Treatment of thallium(I) chloride or bromide with ethylmagnesium bromide in ether (104) or tetrahydrofuran/benzene (86), respectively, gives diethylthallium bromide; addition of ethyl bromide and ethylmagnesium bromide to thallium(I) bromide in pure tetrahydrofuran, however, results in formation of tri-

ethylthallium (120). Aromatic Grignard reagents which do not possess ortho substituents react with thallium(I) bromide in tetrahydrofuran/benzene solvent to give biaryls in high yield (87). This process has been developed into a simple and convenient preparative method for the synthesis of biaryls. Mechanisms have been proposed for the above reactions which involve initial formation of organothallium(I) compounds; all attempts to isolate such species, however, have proved unsuccessful (88).

Cyclopentadienylthallium(I) and Related Compounds


In contrast to other organothallium(I) compounds, cyclopentadienylthallium(I) is a remarkably stable compound. Samples can be stored in sealed bottles for months without appreciable decomposition occurring; it is unaffected by water and dilute alkali; and it is only slowly oxidized by air at room temperature. Cyclopentadienylthallium(I) was first prepared by Meister in 1956 by addition of freshly distilled cyclopentadiene to a suspension of thallium(I) sulfate in dilute potassium hydroxide solution (101, 102). A number of variations of this procedure have been described (5, 25, 34, 56), and the compound has been made in other ways (35, 56, 110, 164), but Meister's preparation, in which the yield of crude product is greater than 90%, remains the method of choice. Purification of crude cyclopentadienylthallium(I) is best accomplished by vacuum sublimation, and purity of samples can readily be assessed by gas-liquid chromatography on silicone oil at 170° C using hydrogen as carrier gas (7).

The salt is a colorless crystalline solid which is virtually insoluble in all common organic solvents. It reacts slowly with chloroform and carbon tetrachloride to give thallium(I) chloride (25), gives a characteristic red coloration with carbon disulfide, and undergoes the Diels-Alder reaction with maleic anhydride (110). It is rapidly decomposed by acids, but is stable to water; this latter fact has been interpreted (55) in terms of the small free energy change for the reaction



The structure of cyclopentadienylthallium(I) has been the subject of controversy and while the arguments have not been entirely satisfactorily settled, the evidence now available indicates that the compound is primarily ionic in the solid state but possibly mainly covalent in the gaseous phase. The former conclusion at least is reasonable in view of the well-known stability of the cyclopentadienyl anion. Cyclopentadienylthallium(I) has

zero magnetic moment (36), and the gas-phase infrared spectrum indicates C_{5v} symmetry, i.e., the thallium atom below the plane of the cyclopentadiene ring (25). This conclusion was subsequently confirmed by X-ray studies (37) and by examination of the microwave spectrum (160). The values obtained from the microwave spectrum for the various molecular parameters are summarized in Scheme 1. The structure of the solid material, determined by X-ray analysis, differs from the structure in the gas phase in that it is

	C—H bond length	1.08 Å
	C—C bond length	1.43
	C—Tl bond length	2.705
	Tl-center of ring distance	2.41

Scheme 1

polymeric, with a repeating half-sandwich structure in the form of a zig-zag chain. Mass spectral studies of the vapor, on the other hand, show only the presence of the monomer (14).

Almost all of the other physical evidence available on the structure and properties of cyclopentadienylthallium(I) has been interpreted by different workers in terms of either ionic or completely covalent bonding between thallium and carbon. The far-infrared spectrum shows no band in the 480 cm^{-1} region which can be attributed to a C—Tl stretching frequency, as would be expected if the compound were covalent (40). Fritz has questioned the assignment of ionic character on this basis, however, and argued that the absence of a C—Tl stretching frequency is not inconsistent with a centrally bonded σ - p orbital overlap, as a relatively weak σ -bond from metal to ligand would be expected for the covalent compound (39). Evidence from polarographic studies apparently indicates covalent bonding (41), as the electrical conductivity of a solution of cyclopentadienylthallium(I) in dimethylformamide was 20 times less than that of an equimolar solution of thallium(I) perchlorate, and only 2.5 times that of the solvent. Moreover, the energy of the thallium-ring bond was estimated to be 11.3 kcal/mole, which is less than the iron-ring bond in ferrocene. Molecular orbital calculations carried out by Cotton and Reynolds (25) were interpreted as showing that covalent bonding was of little importance, but this conclusion was later challenged by Shibata, Bartell, and Gavin (139).

The NMR spectrum (114) of the salt in tetrahydrofuran at 34°C consists of a singlet at 5.2τ , again apparently indicating an ionic bond and suggesting,

because of the absence of Tl—H coupling, that bonding is via the *p* orbitals in thallium. Rapid chemical exchange of alkyl groups in trialkylthallium compounds has, however, been established by NMR studies (98) and it has been shown that exchange can be inhibited if the spectra are recorded at low temperatures. Consequently, were cyclopentadienylthallium(I) to be covalent, the singlet observed at 34° C in the NMR spectrum may be the result of rapid exchange between the thallium atoms and the cyclopentadiene rings, and no conclusions as to the nature of the bonding can be drawn from the NMR study until the spectra have been examined at low temperatures.

A number of alkylated and ring-annelated derivatives of cyclopentadienylthallium(I) have been reported. All were prepared by the same procedure used for the parent compound, and relevant experimental data are listed in Table I. None of these compounds is as stable as cyclopentadienylthallium(I); the methyl-substituted derivative, for example, undergoes essentially spontaneous oxidation on exposure to the atmosphere (25), and, qualitatively, the order of stability has been assessed (105) as

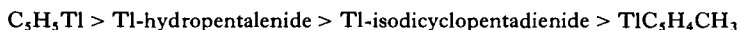
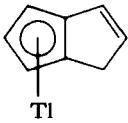
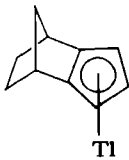


TABLE I

THALLIUM(I) SALTS OF ALKYLATED AND RING-ANNELATED CYCLOPENTADIENES

Salt	Yield (%)	M.p. (° C)	References
Methylcyclopentadienylthallium(I)	76	88–9	25, 135
Ethylcyclopentadienylthallium(I)	86	50–2	114
<i>tert</i> -Butylcyclopentadienylthallium(I)	67	169.8–170	113, 114
1,3-Di- <i>tert</i> -butylcyclopentadienylthallium(I)	19	—	114
$[(\text{C}_6\text{H}_5)_2\text{CHC}_5\text{H}_4\text{Cr}(\text{CO})_3]\text{Tl}$	—	—	21
	100	87–9	62
	—	—	62

There is no ready explanation for the relative instability of the alkyl-substituted cyclopentadienylthallium(I) compounds. The pK_a change in the hydrocarbon substrate, which results from introduction of an alkyl group, is likely to be small and insufficient to account for the dramatic stability differences [in the case of 9-R-substituted fluorenes, for example, where R = H, CH₃, C₂H₅, or *tert*-butyl, the maximum difference in pK_a units between any two compounds is only 1.6 (9)]. The change in orbital overlap caused by introduction of an alkyl group is also likely to be small; the 1,1'-dialkylferrocenes, for example, are stable compounds (137). At present, the only plausible explanation appears to be that the relative stabilities of the crystal lattices vary markedly (169).

Very little is known as yet of the chemistry of cyclopentadienylthallium(I) and the related compounds listed in Table I. The parent compound gives tribromocyclopentane on treatment with bromine and the hexabromo derivative with potassium hypobromite (112). By far the most important use discovered so far for these organothallium(I) compounds is the preparation of metallocenes and cyclopentadiene-transition metal complexes. These preparations are, in general, characterized by manipulative simplicity and high yields, and details of the reactions reported thus far are summarized in Tables II-IV.

TABLE II

PREPARATION OF METALLOCENES FROM CYCLOPENTADIENYLTHALLIUM(I)

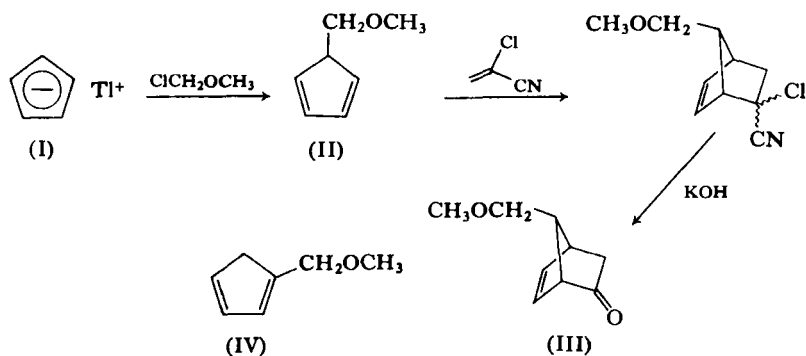
Co-reagent	Product	Yield (%)	References
FeCl ₂	Ferrocene	87	25
		70	56
		68	115
FeCl ₃	Ferrocene	96	115
CoCl ₂	Cobaltocene	83	56
NiBr ₂	Nickelocene	26	56
		20	115
Ni(NH ₃) ₆ Cl ₂	Nickelocene	70	116
HgCl ₂	Dicyclopentadienylmercury	97.5	115

The potential utility of cyclopentadienylthallium(I) in organic synthesis, and its advantages over the much more commonly employed sodium salt, have been illustrated recently (22). Treatment of (I) (Scheme 2) with chloromethyl methyl ether in dry ether resulted in smooth monoalkylation

TABLE III

PREPARATION OF TRANSITION METAL COMPLEXES FROM CYCLOPENTADIENYLTHALLIUM(I)

Co-reagent	Product	Yield (%)	References
$(\text{CH}_3)_3\text{SiCl}$	$\text{C}_5\text{H}_5\text{Si}(\text{CH}_3)_3$	23	113
TiCl_4	$(\text{C}_5\text{H}_5)_2\text{TiCl}_2$	61	56
CrCl_3 followed by NO	$\text{C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{Cl}$	—	115
$\text{Mn}(\text{CO})_5\text{Cl}$	$\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$	93	108
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_3\text{I}$	$[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$	—	64
$\text{C}_2\text{F}_5\text{Fe}(\text{CO})_4\text{I}$	$\text{C}_2\text{F}_5\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$	—	65
$(\text{CF}_3)_2\text{CFFe}(\text{CO})_4\text{I}$	$(\text{CF}_3)_2\text{CFFe}(\text{CO})_2\text{C}_5\text{H}_5$	70	65
$\text{C}_3\text{F}_7\text{Fe}(\text{CO})_4\text{I}$	$\text{C}_3\text{F}_7\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$	—	64
CoBr_2 followed by Br_2	$(\text{C}_5\text{H}_5)_2\text{CoBr}_3$	100	115
$\text{C}_5\text{H}_5\text{Co}(\text{CO})\text{I}_2$	$[(\text{C}_5\text{H}_5)_2\text{Co}]^+$	—	64
ZrCl_4	$(\text{C}_5\text{H}_5)_2\text{ZrCl}_2$	52	113
$[\text{Mo}(\text{NO})_2\text{Cl}_2]_n$	$\text{C}_5\text{H}_5\text{Mo}(\text{NO})_2\text{Cl}$	25	64
$[\text{C}_5\text{H}_5\text{Mo}(\text{NO})\text{I}_2]_2$	$(\text{C}_5\text{H}_5)_3\text{MoNO}$	65	16, 24
$[\text{C}_5\text{H}_5\text{Mo}(\text{NO})_2\text{I}_2]_2$	$(\text{C}_5\text{H}_5)_2\text{Mo}(\text{NO})\text{I}$	64–79	64
$(\text{CH}_3\text{OC}_{10}\text{H}_{12}\text{PdCl})_2^a$	$\text{CH}_3\text{OC}_{10}\text{H}_{12}\text{PdC}_5\text{H}_5$	65	56
$(\text{C}_8\text{H}_{12}\text{acac})_2\text{Pd}_2\text{Cl}_2^b$	$\text{C}_8\text{H}_{12}\text{acacPdC}_5\text{H}_5$	—	59
HfCl_4	$(\text{C}_5\text{H}_5)_2\text{HfCl}_2$	58	113
$\text{Re}(\text{CO})_5\text{Cl}$	$\text{C}_5\text{H}_5\text{Re}(\text{CO})_3$	60	109
$(\text{CH}_3\text{OC}_{10}\text{H}_{12}\text{PtCl})_2^c$	$\text{CH}_3\text{OC}_{10}\text{H}_{12}\text{PtC}_5\text{H}_5$	69	56
$(\text{C}_8\text{H}_{12}\text{acac})_2\text{Pt}_2\text{Cl}_2^d$	$\text{C}_8\text{H}_{12}\text{acacPtC}_5\text{H}_5$	—	59

^a Di- μ -chloro-bis(methoxydicyclopentadiene)dipalladium(II).^b Di- μ -chloro-bis(2-acetylacetonylcyclooct-5-en-yl)palladium(II).^c Di- μ -chloro-bis(methoxydicyclopentadiene)diplatinum(II).^d Di- μ -chloro-bis(2-acetylacetonylcyclooct-5-en-yl)platinum(II).

Scheme 2

TABLE IV
PREPARATION OF TRANSITION METAL COMPLEXES FROM ALKYL-SUBSTITUTED AND RING-ANNELATED
CYCLOPENTADIENYLTHALLIUM(I) COMPOUNDS

Reagents	Product	Yield (%)	References
$C_2H_5C_5H_4Tl/CoBr_2/Br_2/H_2PtCl_6$	$[(C_2H_5C_5H_4)_2Co]_2^{2+}PtCl_6^{2-}$	74	117
$t-C_4H_9C_5H_4Tl/CoBr_2/Br_2$	$[(t-C_4H_9C_5H_4)_2Co]^+Br_3^-$	65	117
$1,3-Di-t-C_4H_9C_5H_3Tl/CoBr_2/Br_2$	$[(1,1',3,3'-tetra-t-C_4H_9C_5H_3)_2Co]^+Br_3^-$	64	117
$t-C_4H_9C_5H_4Tl/ZrCl_4$	$(t-C_4H_9C_5H_4)_2ZrCl_2$	76	113
Tl-hydropentalenide/ $FeCl_2$	Bis(hydropentalenyl)iron	49	62
Tl-hydropentalenide/cycloocta- 1,5-dienerhodium chloride	Cyclopentadienylcycloocta- 1,5-dienerhodium	76	62
Tl-hydropentalenide/ $(CH_3)_3PtI$	Hydropentalenyl-Pt $(CH_3)_3$	43	62
Tl-isodicyclopentadienide/ $FeCl_2$	Bis(isodicyclopentadienyl)iron	20	62

to give (II), which was converted into the ketone (III), a precursor in the syntheses of the six primary prostaglandins. Under the essentially neutral reaction conditions during alkylation, relatively little isomerization of (II) to (IV) occurred; with either the sodium or lithium salt of (I), however, isomerization of II to the undesired product (IV) represented a serious experimental problem. Similar results have been obtained using a variety of active alkylating reagents (23), and as a result of these preliminary experiments further studies on the alkylation of cyclopentadienylthallium(I) should prove fruitful.

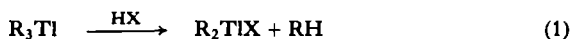
III

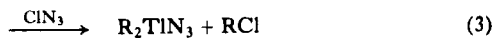
ORGANOTHALLIUM(III) COMPOUNDS

A. Preparation and Properties of R_3Tl Compounds

Only about a dozen R_3Tl compounds have been reported as yet (73), and there have been no systematic studies of their properties or reactions. As described previously (see Section II) trimethylthallium and triphenylthallium have been prepared by treatment of thallium(I) iodide with methyl-lithium and phenyllithium, respectively, but the generality of this synthetic method has not been explored. Reaction of diorganothallium(III) compounds R_2TlX with organolithium reagents appears to be a more convenient and widely applicable procedure which, by variation of the organolithium employed, affords access to mixed compounds R_2TlR' (6, 45, 50, 136). Early attempts to effect the analogous reaction of R_2TlX compounds with Grignard reagents in diethyl ether were unsuccessful. Tris(pentafluorophenyl)-thallium has, however, been prepared recently in this manner (30, 132), while use of tetrahydrofuran as solvent has been shown to result in smooth conversion of diethylthallium bromide into triethylthallium on treatment with ethylmagnesium bromide (120).

The most outstanding feature of R_3Tl compounds with respect to chemical reactivity is the great ease with which one of the substituent groups may be displaced and R_2TlX compounds formed. Cleavage has been found to occur readily not only with a wide variety of proton acids (82) [Eq. (1)], but with halocarbons (82) [Eq. (2)], pseudohalogens (106) [Eq. (3)], and





sulfur dioxide (80) [Eq. (4)]. These data are consistent with the fact that the Tl—C bonds in R_3Tl are believed to be very weak with respect to the first dissociation. In trimethylthallium, for example, the dissociation energy for the first Tl—C bond has been estimated to be only 27.4 kcal/mole (57). Moreover, the products of the reactions are ionic R_2TlX compounds in which the linear cation RTl^+R , which is isoelectronic with mercury(II) and is *sp*-hybridized, is known to be particularly stable (73, 78). Consequently, cleavage of the second and third C—Tl bonds in R_3Tl compounds does not normally occur easily, and requires fairly vigorous reaction conditions such as exposure to ultraviolet light or treatment with halogens (for further discussion see Section II,B).

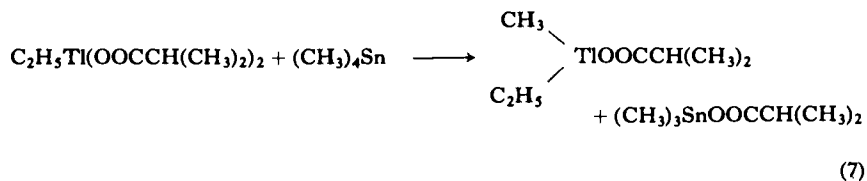
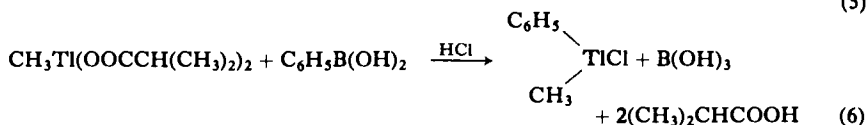
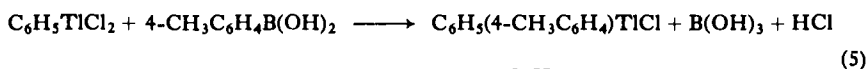
The weak C—Tl bond in R_3Tl compounds and the stability of R_2TlX compounds are thus the two major reasons for the high chemical reactivity of triorganothallium derivatives. It has been suggested in the past that their reactivity is due to a tendency to ionize to $\text{R}_2\text{Tl}^+\text{R}^-$ (51), but there is no evidence to support the presence of carbanionic species in the absence of a co-reagent. Trimethylthallium, which is associated in the solid state (138), exists as the monomer both in the vapor state and in benzene solution (43, 146). Association in the crystal results from unsymmetrical bridging of the thallium atoms by the methyl groups (138), and this bridging is a weak interaction. Methyl bridging to give dimers has been invoked to account for the rapid intermolecular exchange of methyl groups which has been observed in the NMR spectrum of trimethylthallium (98). In view of the absence of any physical evidence for carbanionic character in R_3Tl compounds, therefore, the facile cleavage of the first C—Tl bond can be regarded as the result of a simple concerted substitution process.

B. Preparation and Properties of R_2TlX Compounds

These compounds are the most stable of the three classes of organothallium(III) derivatives and have been prepared by a wide variety of classical organometallic procedures. Many exchange reactions of TlX_3 ($\text{X} = \text{Cl}$, carboxylate) with organo derivatives of boron, mercury, tin, lead, etc., have been shown to result in formation of R_2TlX compounds (73, 78), but are of relatively little preparative significance. The most frequently used procedure

for the preparation of R_2TlX compounds consists of treatment of a thallium(III) halide or carboxylate with excess of Grignard reagent (73, 78). Due to oxidation of the Grignard reagent by thallium(III), yields of products are generally moderate and vary with the nature of the Grignard reagent. Thus yields of R_2TlX derivatives are reasonable when $RMgCl$ or $RMgBr$ is used, but considerably lower when $RMgI$ is employed. In contrast to most of the other procedures that have been described, however, the low yields encountered with this method are often acceptable as the starting materials are readily accessible.

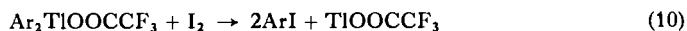
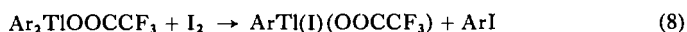
A simple, high-yield procedure for the conversion of $ArTlX_2$ into Ar_2TlX compounds has recently been described (90). This symmetrization reaction, the mechanism of which is not known, can be effected by treatment of the $ArTlX_2$ compound either with triethyl phosphite or with hot aqueous acetone. As a wide variety of $ArTlX_2$ compounds can now be easily prepared by electrophilic thallation of aromatic substrates with thallium(III) trifluoroacetate (*q.v.*), symmetrization represents the method of choice for the preparation of the majority of Ar_2TlX compounds. Only about twenty "mixed" compounds, $RR'TlX$, have been prepared so far, and the only general synthetic procedure available consists of a disproportionation reaction between an $RTlX_2$ species and another organometallic reagent [e.g., Eqs. (5)–(7)].



There appears to be a widespread belief that compounds of the general type R_2TlX are among the most stable and the least reactive of organothallium derivatives and, indeed, among organometallic compounds in general (73, 79). This misconception would appear to be due primarily to a paucity of information stemming from disinterest on the part of previous

investigators, for recent investigations (149) have indicated that Ar_2TiX compounds are useful and versatile intermediates for the preparation of a variety of substituted aromatic compounds.

Specifically, it has recently been found (149) that diarylthallium trifluoroacetates may be converted into aromatic iodides by refluxing a solution in benzene with an excess of molecular iodine. Yields are excellent (74–94%) and the overall conversion represents, in effect, a procedure for the conversion of aromatic chlorides or bromides into aromatic iodides via intermediate Grignard reagents. The overall stoichiometry for this conversion is represented in Eq. (10), and it would appear that the initial reaction is probably formation of 1 mole of aromatic iodide and 1 mole of arylthallium trifluoroacetate iodide [Eq. (8)] which subsequently spontaneously decomposes to give a second mole of aromatic iodide and thallium(I) trifluoroacetate [Eq. (9)]. Support for this interpretation comes from the

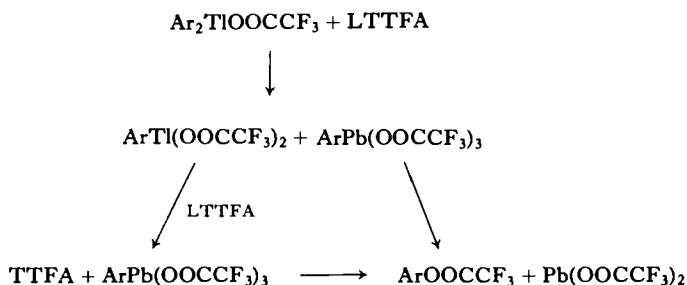


observation that treatment of di-*p*-tolylthallium trifluoroacetate with 1 equivalent of iodine resulted in the formation of 2 equivalents of *p*-iodotoluene (91%) and thallium(I) trifluoroacetate (88%); no thallium(I) iodide could be detected. The spontaneous disproportionation of arylthallium trifluoroacetate iodides to aromatic iodides has been confirmed independently (2).

The conversion of diarylthallium trifluoroacetates to aromatic iodides by treatment with molecular iodine is thus analogous to the well-known conversion of diarylmercury derivatives with iodine to a mixture of an aromatic iodide and an arylmercury iodide (134), but it is much more effective as a synthetic tool because of the spontaneous disproportionation to product of the intermediate arylthallium trifluoroacetate iodide. The present procedure thus provides a practical synthetic method for the ultimate conversion of aryl Grignard reagents to aromatic iodides.

It has been reported previously (147), and will be discussed in detail later, that arylthallium ditrifluoroacetates may be converted in good yield to phenols by treatment with lead tetraacetate in trifluoroacetic acid solution followed by addition of 1 mole of triphenylphosphine. The immediate product of the above reaction, an aryl trifluoroacetate, is hydrolyzed

quantitatively to the desired phenol with aqueous alkali. The same reaction sequence may be applied to diarylthallium trifluoroacetates; phenols are formed in comparable yields (20–70%). The overall reaction probably involves cleavage of the diarylthallium trifluoroacetate to give an arylthallium ditrifluoroacetate and an aryllead tris(trifluoroacetate). The latter presumably decomposes spontaneously to lead ditrifluoroacetate and the aryl trifluoroacetate, while the former undergoes a metal–metal exchange with lead tetratrifluoroacetate (via an intermediate complex which can be isolated) to give a second mole of an aryllead tris(trifluoroacetate).



The reason for the effectiveness of triphenylphosphine is at present uncertain, although its eventual isolation as triphenylphosphine oxide indicates that it may well function as a scavenger for the thallium(III) released in the metal–metal exchange reaction.

This phenol synthesis complements the analogous reaction (see below) from arylthallium ditrifluoroacetates (147). Although yields are only moderate, the procedure represents a viable conversion of aryl Grignard reagents to phenols. It is a practical method, however, only when the diarylthallium trifluoroacetate precursor is formed via the Grignard route; the alternative synthesis via symmetrization of arylthallium ditrifluoroacetates is obviously circuitous, since the latter compounds may be converted directly to phenols.

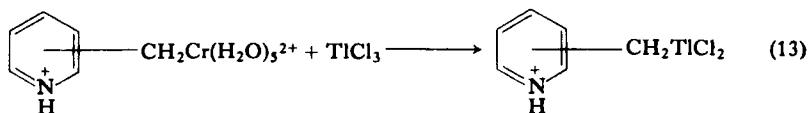
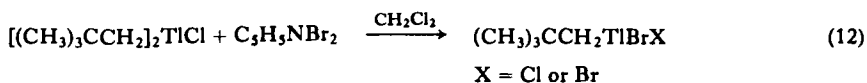
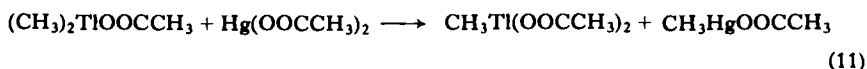
It has been reported that photolysis of arylthallium ditrifluoroacetates in benzene suspension results in replacement of the thallium substituent by a phenyl group (i.e., phenylation) to give unsymmetrical biphenyls in excellent yield (152); this reaction is summarized in Section III, C. An analogous reaction occurs upon photolysis of diarylthallium trifluoroacetates in benzene suspension: unsymmetrical biphenyls are formed in comparable yield (40–95%). The mechanism of this conversion is undoubtedly similar to that

discussed in Section III,C for the conversion of arylthallium ditrifluoroacetates to biphenyls. The two syntheses complement each other, since the substituent pattern possible with diarylthallium trifluoroacetates prepared via the Grignard route may be different from that accessible via the symmetrization route (which must be identical to the pattern present in the initial arylthallium ditrifluoroacetate precursors).

From these limited observations it would appear that Ar_2TlX compounds are not as stable as current mythology would have us believe, and that they may be utilized under appropriate reaction conditions as intermediates in various aromatic substitution reactions. Further investigations of these compounds are clearly warranted.

C. Preparation and Properties of RTlX_2 Compounds

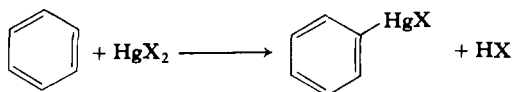
Monoalkylthallium(III) compounds are unstable (73, 79), and very few examples of this class have been isolated. A number of alkylthallium diacetates have been obtained either from oxythallation of olefins with thallium(III) acetate (see below) or from exchange reactions such as that shown in Eq. (11) (74, 75). Only four alkylthallium dihalides have been isolated so far, namely a neopentylthallium dihalide (60) [Eq. (12)] and the isomeric 2-, 3-, and 4-pyridiomethylthallium dichlorides (20) [Eq. (13)]. Monoaryl- and monovinylthallium(III) derivatives are considerably more stable than



the corresponding alkyl compounds, and can usually be isolated and characterized without difficulty. Both types of compound have been prepared by exchange reactions between thallium(III) halides or carboxylates and organo derivatives of mercury or tin (73, 79); ArTlX_2 compounds have been prepared similarly from arylboronic acids and thallium(III) halides (73, 79). The synthetic utility of these exchange reactions is obviously

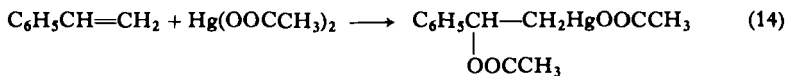
contingent on the accessibility of the requisite organo-mercury, -tin, or -boron derivative, however, and not surprisingly the number of organothallium compounds which has been prepared in this way is rather small. By far the most simple and general procedures for the preparation of monoalkyl- and monoarylthallium(III) compounds are via the oxythallation (66) and thallation reactions, respectively (67).

The general term *metallation* describes that process in which reaction of an unsaturated system with a metal or an electrophilic metal salt results in formation of an unsaturated organometallic compound by formal replacement of a C—H bond by a C—metal bond, as for example in the mercuration of benzene (Scheme 3). The term *oxymetallation* is used to describe the



Scheme 3

overall addition reaction which occurs when unsaturated systems, in particular olefins, are treated with electrophilic metal salts. Oxymetallation results in formation of *two* bonds and, in the case of olefins, production of saturated organometallic derivatives, as for example in the oxymercuration of styrene [Eq. (14)]. In oxymercuration and oxythallation it has been



shown that addition is not synchronous, that some positive charge can develop on the carbon atom α to the carbon-metal bond during reaction, and that solvent may participate in the addition reaction if it is more nucleophilic than the anion of the metal salt (66, 67, 124). The products obtained from oxymercuration and oxythallation are those derived from Markownikov addition of the electrophile to the double bond.

Metallation and oxymetallation reactions have been observed with the salts of only a few metals, namely mercury(II) (66, 67), thallium(III) (66, 67), lead(IV) (66, 67), palladium(II) (100), gold(III) (63), and platinum(II) (29). These facts correlate well with what Chatt (1) has termed "class b," and Pearson (130) has called "soft acid" character. Soft acids are characterized by low charge, large size, and, often, *d* electrons in their outer shell. No "class b" metal is known, in fact, which contains fewer than five *d*

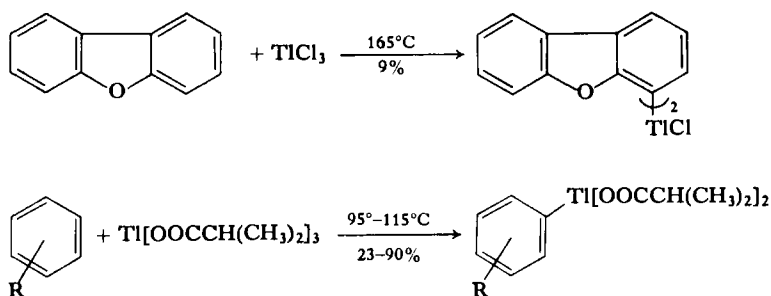
electrons. On the basis of these facts, thallium(III) should be a softer acid than thallium(I), and this has been found to be the case (131). The above features characteristic of metallation reactions were first recognized by Davidson and Triggs (29). More recently, an attempt has been made by Klopman (69) to estimate "softness" quantitatively using a frontier orbital calculation approach, and some of the results obtained for metal ions are shown in Table V. These data not only confirm that thallium(III) is softer

TABLE V
CALCULATED SOFTNESS CHARACTER (E_n)
OF SELECTED METAL CATIONS

Metal cation	E_n	
Al ³⁺	6.01	Hard
Fe ³⁺	2.22	
Ga ³⁺	1.45	Borderline
Tl ¹⁺	-1.88	
Ag ¹⁺	-2.82	Soft
Tl ³⁺	-3.37	
Hg ²⁺	-4.62	

than thallium(I), but also indicate that thallium(III) salts, unlike gallium(III) salts, should be almost as reactive as mercury(II) salts in metallation and oxymetallation reactions.

In contrast to the enormous amount of effort which has been devoted to studies of the mercuration (67) and oxymercuration (66) processes, the analogous reactions involving thallium(III) salts have been virtually ignored. The first example of electrophilic aromatic thallation was recorded in 1943 by Gilman and Abbott (42), who found that treatment of dibenzofuran with thallium(III) chloride at 165°C gave di-4-(benzofuryl)thallium(III) chloride in 9% yield (Scheme 4). More than ten years later Glushkova and Kocheshkov (46) reported that reaction of activated aromatic substrates with thallium(III) isobutyrate at 95°–115°C led to formation of arylthallium diisobutyrate (Scheme 4); similar results have since been claimed with respect to thallium(III) acetate (29). As synthetic routes to ArTlX₂ compounds, however, these reactions are less than satisfactory. The thallium(III) salts which were used are all poorly electrophilic, especially the chloride, and hence the range of aromatic substrates which can be effectively substituted



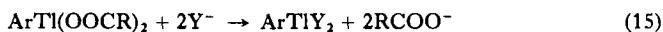
Scheme 4

is severely restricted. Moreover, many ArTlX_2 compounds are thermally unstable, and undergo decomposition and/or symmetrization on heating (see Section III,B); the rather high reaction temperatures necessary in the above procedures are therefore undesirable. The deleterious effect of high temperature is in fact illustrated in Gilman and Abbott's work (Scheme 4); the product isolated was not that which would be expected from an electrophilic aromatic substitution reaction, namely the monoarylthallium(III) derivative, but the more stable diarylthallium chloride. This latter compound was presumably formed by thermal symmetrization of the initially formed ArTlCl_2 derivative.

Thallium(III) trifluoroacetate (hereafter abbreviated TTFA), in contrast to the acetate, isobutyrate, and chloride, is a highly ionic salt, and has been found to be an extremely reactive thallating reagent (89). This particular salt was selected for thallation by analogy with results obtained in mercuration, where Brown and Wirkkala (13) found that use of trifluoroacetic acid (hereafter abbreviated as TFA) as solvent resulted in a rate increase in electrophilic aromatic mercuration of 6.8×10^5 relative to acetic acid. Treatment of aromatic compounds with TTFA in either TFA or, for acid-sensitive compounds, in a solvent such as acetonitrile results in direct thallation and formation of arylthallium ditrifluoroacetates. Reaction with substrates which are activated toward electrophilic substitution is generally complete within a few minutes at room temperature, and in the majority of cases the arylthallium ditrifluoroacetates crystallize from the reaction mixture. Thallation of mildly deactivated substrates such as the halo-benzenes requires longer reaction times at room temperature (~ 48 hours) or 30 minutes at reflux temperature (73°C) in TFA, while deactivated compounds such as benzoic acid are thallated after ~ 24 -hour reflux in

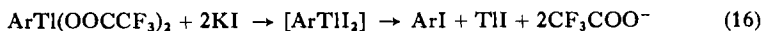
TFA. Electrophilic aromatic thallation with TTFA therefore constitutes a simple and general procedure for the preparation of monoarylthallium(III) derivatives and has been the subject of detailed kinetic, mechanistic, and synthetic investigations. These aspects of the thallation reaction are discussed at length below.

The properties of ArTlX_2 compounds vary erratically with the nature of X, although the reasons for this behavior are not yet understood. The halides ArTlF_2 and ArTlCl_2 appear from both conductance experiments (32, 81) and infrared studies (81) to be largely covalent while, by use of similar techniques, it has been shown that the carboxylate salts $\text{ArTl}(\text{OOCR})_2$ [$\text{R} = \text{CH}_3, \text{CH}(\text{CH}_3)_2, \text{CF}_3$] are partially or completely ionic (81). Consequently, treatment of arylthallium dicarboxylates with inorganic nucleophiles Y^- results in most cases in simple displacement of the carboxyl group and formation of the corresponding ArTlY_2 compound [Eq. (15)] (9). As arylthallium ditrifluoroacetates are readily accessible via thallation of



aromatic compounds with TTFA, this procedure therefore constitutes a general method for the preparation of ArTlY_2 compounds.

The dramatic variation in the stability of these organothallium compounds is well illustrated by the halides ArTlY_2 , where $\text{Y} = \text{F}, \text{Cl}, \text{Br}, \text{I}$. Thus, treatment of arylthallium ditrifluoroacetates with aqueous potassium fluoride, chloride, or bromide results in formation of the corresponding arylthallium dihalides (90). The fluorides and chlorides are stable, crystalline solids which show little tendency either to disproportionate or to decompose at room temperature. The bromides, on the other hand, are quite unstable and decompose either on storage or on gentle heating ($\sim 40^\circ \text{C}$) to give mainly the aromatic bromide and thallium(I) bromide, together with a small amount of diarylthallium bromide. Treatment of an arylthallium ditrifluoroacetate with aqueous potassium iodide results in direct, and in most cases instantaneous, formation of the corresponding aromatic iodide and thallium(I) iodide (91), presumably via formation of an unstable arylthallium diiodide [Eq. (16)]. All attempts to isolate or intercept arylthallium



diiodides in these reactions have proved unsuccessful. Organothallium compounds of the type ArTlI_2 are in fact unknown except as complexes where $\text{Ar} = \text{C}_6\text{F}_5$ (30), while the instability of TlI_3 itself is well documented (26).

From the above data it is obvious that the reaction sequence of thallation followed by treatment of the resulting arylthallium ditrifluoroacetate with potassium iodide represents a rapid and extremely simple synthesis of aromatic iodides. Critical to the practical exploitation of this facile aromatic substitution reaction sequence was the *orientation* of the entering iodine with respect to the displaced thallium substituent. Careful investigation has shown that, in all cases, the entering iodine substituent always replaces thallium on the same position on the aromatic ring. Evidence for this conclusion comes not only from the constancy of isomer ratios observed when thallium is replaced by a variety of different substituent groups (see below), but also by NMR spectroscopy. It has been demonstrated previously that thallium-hydrogen coupling constants are approximately 130 times greater than the corresponding hydrogen-hydrogen coupling constants, a phenomenon which has been discussed in detail and qualitatively rationalized on the basis of a Fermi contact interaction arising from the large effective nuclear charge on the thallium atom (98, 99). NMR spectra of ArTlX_2 compounds therefore unambiguously position the thallium with respect to other substituents on the aromatic ring, and careful comparisons of the structures of the starting ArTlX_2 compounds with the resulting aromatic iodides fully justify the above conclusion.

With the $\text{ArH} \rightarrow \text{ArTlX}_2 \rightarrow \text{ArI}$ reaction sequence available as a rapid and reliable probe for aromatic thallation, a detailed study was undertaken of the various factors affecting orientation in this electrophilic metallation process (153). The results, which are summarized below, demonstrate that aromatic thallation is subject to an almost unprecedented degree of orientation control; coupled with the ease with which thallium can then be displaced by other substituent groups (this aspect of the synthetic exploitation of aromatic thallation is discussed in detail below), the sequential processes of thallation followed by displacement represent a new and versatile method for aromatic substitution which both rivals and complements the classic Sandmeyer reaction.

Aromatic thallation has been shown to be a *reversible* electrophilic substitution reaction with an energy of activation of approximately 27 kcal/mole and an extremely large steric requirement (153). The consequence of the latter feature of aromatic thallation is that there is a significant preference for para substitution in thallation of simple monosubstituted benzenoid compounds. It will be seen by examination of Table VI that the amount of para substitution increases as the size of the substituent increases (for

example, the amount of para substitution observed on thallation of toluene, *n*-propylbenzene, and cumene is 87, 91, and 94%, respectively). Examination of the table further reveals, however, that the orientation of the incoming thallium electrophile can be dramatically influenced by substituents on the aromatic ring capable of complexing with thallium. A dramatic illustra-

TABLE VI

ISOMER DISTRIBUTIONS IN THE THALLATION OF AROMATIC
COMPOUNDS AT ROOM TEMPERATURE

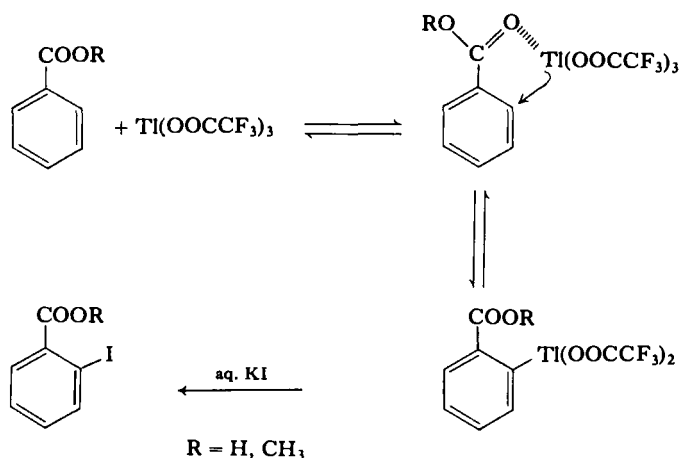
Substrate C ₆ H ₅ R, R =	Isomer distribution ^a		
	<i>Ortho</i>	<i>Meta</i>	<i>Para</i>
CH ₃	9	4	87
CH ₂ CH ₂ CH ₃	3	6	91
CH(CH ₃) ₂	1	5	94
COOH	95	5	0
CH ₂ COOH	92	3	5
CH(CH ₃)COOH	65	11	24
C(CH ₃) ₂ COOH	0	37	63
CH ₂ CH ₂ COOH	29	13	58
CH(CH ₃)CH ₂ COOH	37	14	49
CH ₂ CH ₂ CH ₂ COOH	6	10	84
CH ₂ CH ₂ CH ₂ CH ₂ COOH	5	9	86
COOCH ₃	95	5	0
CH ₂ COOCH ₃	92	3	5
CH ₂ CH ₂ COOCH ₃	53	7	40
CH ₂ OH	>99	—	—
CH ₂ OOCCH ₃	50	21	29
CH ₂ CH ₂ OH	83	6	11
CH ₂ CH ₂ OOCCH ₃	3	13	84
CH ₂ CH ₂ CH ₂ OOCCH ₃	5	12	83
OCH ₃	7	—	93 ^b
CH ₂ OCH ₃	>99	—	—
CH ₂ CH ₂ OCH ₃	85	3	12
CH ₂ CH ₂ CH ₂ OCH ₃	27	6	67
CH ₂ OOCCH ₃	49	24	27
OCOCH ₃	21	—	79
<i>o</i> -CH ₃ C ₆ H ₄ CH ₂ COOH	31% thallation in position 6 ^c		

^a Determined by glc analysis of the corresponding aromatic iodides.

^b Determined by NMR. Thallation was carried out at -25°C.

^c Exact values for the percentage of thallation in the other positions were not obtained.

tion of this effect is the almost exclusive (95%) ortho substitution observed with benzoic acid or with methyl benzoate. The rationalization for this dramatic reversal in the normal orientation rules (ortho substitution with a meta-directing substituent) is intramolecular delivery of the thallium electrophile to the ortho position through an intermediate substrate–electrophile complex (Scheme 5). Thallation of phenylacetic acid (or its esters) likewise gave almost exclusive ortho substitution, whereas thallation

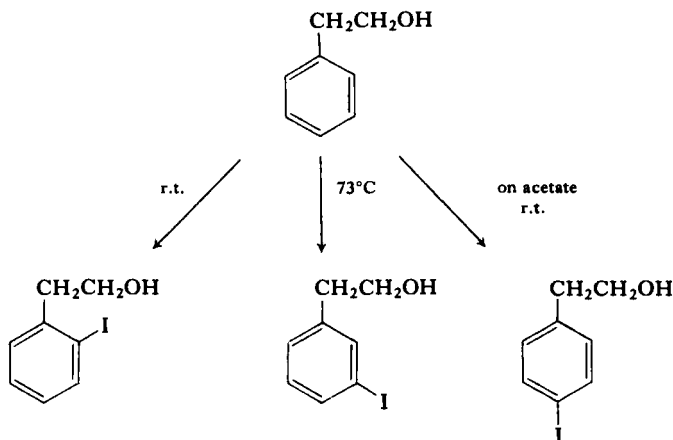


Scheme 5

of 3-phenylpropanoic acid gave only 30% ortho substitution. Apparently intramolecular delivery of thallium can occur to the ortho position through a five- or six-membered chelate ring, but the seven-membered chelate ring formed with 3-phenylpropanoic acid is too large to allow ortho substitution. These preliminary conclusions were confirmed by examination of the thallation–iodination sequence with a number of homologous series of compounds substituted in the side chain with substituents capable of complexing with TTFA, the electrophile employed in all these studies. Independent of the nature of the complexing group (carboxylic acid, carboxylic ester, alcohol, ether, acetate), five- and six-membered intermediate chelates led to exclusive or predominate ortho substitution, while increasing the size of the intermediate chelate by increasing further the distance of the complexed electrophile from the aromatic ring resulted in a sharp decrease in ortho substitution.

A dramatic illustration of the practical application of these observations is seen in the thallation-iodination of phenylethanol versus the acetate of phenylethanol; the former gives *o*-iodophenylethanol, while the latter gives *p*-iodophenylethanol.

Kinetic studies, as mentioned above, show that aromatic thallation is a freely reversible electrophilic substitution reaction with an activation energy of approximately 27 kcal/mole. The principle of microscopic reversibility predicts that, *under equilibrating conditions*, the meta isomer should accumulate at the expense of the kinetically favored ortho and para isomers, at least to the point of statistical distribution (as a consequence of the steric preference for para versus ortho substitution, this statistical distribution turns out to be 33% para, 66% meta). In agreement with this prediction, it has been found that the amount of *m*-iodocumene is increased 17-fold by carrying out the thallation of cumene at the temperature of refluxing TFA (73°C) rather than at room temperature prior to quenching of the reaction mixture with aqueous potassium iodide. Thus thallation of phenylethanol at 73°C followed by addition of potassium iodide gives predominantly *m*-iodophenylethanol; coupled with the results described above, it will be seen that, under appropriate conditions but utilizing the same substrate and the same reagents, selective ortho, or meta, or para substitution can be achieved (Scheme 6). This degree of control over orientation in aromatic substitution reactions is unprecedented.



Scheme 6

Reaction with TTFA/TFA (at temperature indicated) followed by addition of aqueous KI.

In summary, then, the orientation of electrophilic thallation can be controlled by an appropriate manipulation of reaction conditions. Under conditions of kinetic control, ortho substitution results when chelation of the electrophilic reagent (TTFA in the studies described above) with the directing substituent permits intramolecular delivery of the electrophile, and para substitution results when such capabilities are absent; this latter result is an expression of the very large steric requirements of the bulky thallium electrophile. Under conditions of thermodynamic control, however, meta substitution is observed.

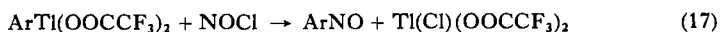
From the point of view of the synthetic organic chemist, the importance of aromatic thallation, and the remarkable degree of orientation control which can be exercised over this process, lies in the ease with which the resulting ArTlX_2 compounds can be converted into substituted aromatic derivatives in which the new substituent group has entered the ring at the position to which thallium was originally attached. Syntheses of phenols, nitroso compounds, biaryls, aromatic nitriles, thiophenols, and deuterated aromatic compounds have all been achieved; these results are summarized briefly below.

Transmetallation reactions involving thallium(III) carboxylates and diarylmercury compounds (47, 61, 85), arylthallium dicarboxylates and dihalomercury compounds (48), lead(IV) carboxylates and diarylmercury compounds (28, 85), and mercury(II) carboxylates and diaryllead dicarboxylates (129) have all been reported. Coupled with the knowledge that aryllead tricarboxylates are unstable and disproportionate, at least in part, to give arylacetates (133), it might be expected that ArTlX_2 compounds would undergo transmetallation with lead(IV) carboxylates. More specifically, since transmetallation is apparently an electrophilic substitution reaction on the original aryl-metal bond (28), such a transmetallation could be facilitated by the use of lead tetratrifluoroacetate as the electrophilic reagent. Furthermore, the subsequent decomposition of the anticipated product of such a transmetallation reaction, the aryllead trifluoroacetate, should undergo spontaneous decomposition to an aryl trifluoroacetate (i.e., a phenol by subsequent hydrolysis). These expectations have been thoroughly confirmed in a new and practical phenol synthesis from arylthallium ditrifluoroacetates (147). Thus, treatment of the latter intermediates in trifluoroacetic acid solution with 1 equivalent of lead tetraacetate (which is converted *in situ* to lead tetratrifluoroacetate) leads to the formation of aryltrifluoroacetates, which are hydrolyzed with dilute alkali to give the desired phenols. When aryl-

thallium ditrifluoroacetates recrystallized to isomeric purity are employed, isomerically pure phenols result in 30–80% yield. On the other hand, the entire reaction sequence involving thallation, transmetallation, decomposition to the aryltrifluoroacetates, and hydrolysis can be carried out in a single step directly from the aromatic hydrocarbon; the phenols resulting reflect the isomer distribution originally achieved in the initial thallation process. In optimum cases, this one-step sequence, which proceeds in 20–65% yield, represents an extremely convenient method for the direct introduction of hydroxyl groups into aromatic nuclei.

Yields in the above reactions can often be improved by the addition of 1 mole of triphenylphosphine directly to the trifluoroacetic acid solution of the reactants immediately before final work-up. It would appear that the triphenylphosphine functions as a scavenger for TTFA released in the metal–metal exchange reaction, thus protecting the final phenol from further electrophilic thallation and/or oxidation. Validation of the metal–metal exchange mechanism was obtained indirectly by isolation and characterization of an $\text{ArTlX}_2/\text{LTTFA}$ complex directly from the reaction mixture. NMR analysis revealed that this complex still possessed an intact aryl–thallium bond, indicating that it was probably the precursor to the transmetallation products, an aryllead tris(trifluoroacetate) and TTFA.

Arguing by analogy with results obtained and discussed for mercury–lead exchange reactions (28), the above transmetallation reaction involving ArTlX_2 compounds and lead tetratrifluoroacetate probably involves an electrophilic attack by lead(IV) on the aryl–thallium bond. Electrophilic displacement of thallium by other suitable electrophiles might represent a novel method for electrophilic aromatic substitution with unique orientation possibilities, since the final orientation of substituents would presumably be determined by the initial thallation process rather than by the normal rules of electrophilic substitution. This latter point has not as yet been explored, but the validity of the general concept seems to be supported by two further examples of electrophilic cleavage of the aryl–thallium bond. The first is protodethallation, the simplest example of displacement of thallium by an electrophile and a thoroughly studied reaction which forms the basis of the thermodynamic orientation control exercised over electrophilic thallation (see above). The second example involves the reaction of arylthallium ditrifluoroacetates with nitrosyl chloride, a reaction which provides a remarkably facile general route to aromatic nitroso compounds (150). The overall stoichiometric reaction is indicated in Eq. (17); it will be seen that



this is another example of electrophilic displacement of thallium(III) from the aromatic nucleus [release of thallium(III) rather than thallium(I) in this reaction has been confirmed experimentally]. In fact, since the arylthallium ditrifluoroacetates can be recrystallized to isomeric purity, the above reaction constitutes a novel and potentially useful method for the direct introduction of nitrogen functionalities (nitroso, amino, or nitro) into aromatic nuclei with all of the orientation control potential inherent in the initial electrophilic aromatic thallation reaction. Nitroso compounds have been prepared in this way in 40–90% yield from a wide variety of aromatic substrates.

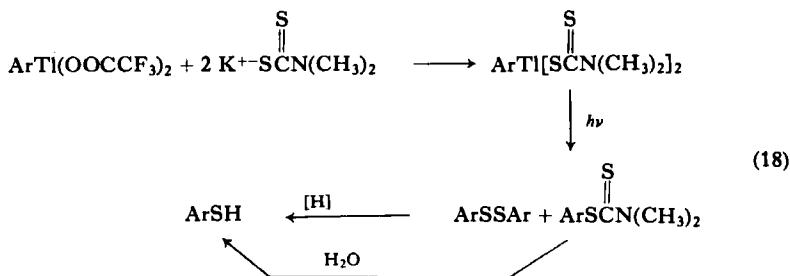
The versatility of ArTlX_2 compounds as intermediates for the synthesis of substituted aromatic compounds has been substantially extended by the observation that the aryl–thallium bond is extremely labile photochemically. The resulting aryl radical can then be captured by appropriate reagents (see below) to give substituted aromatic compounds. A remarkable feature of these photochemical conversions of ArTlX_2 compounds to substituted aromatics is that, as before, the new substituent always enters the ring at the position to which thallium was originally attached.

For example, photolysis of a suspension of an arylthallium ditrifluoroacetate in benzene results in the formation of unsymmetrical biphenyls in high yield (80–90%) and in a high state of purity (152). The results are in full agreement with a free radical pathway which, as suggested above, is initiated by a photochemically induced homolysis of the aryl carbon–thallium bond. Capture of the resulting aryl radical by benzene would lead to the observed unsymmetrical biphenyl, while spontaneous disproportionation of the initially formed $\text{Tl}(\text{II})$ species to thallium(I) trifluoroacetate and trifluoroacetoxy radicals, followed by reaction of the latter with aryl radicals, accounts for the very small amounts of aryl trifluoroacetates formed as by-products. This route to unsymmetrical biphenyls thus complements the well-known Wolf and Kharasch procedure involving photolysis of aromatic iodides (171). Since the most versatile route to the latter compounds involves again the intermediacy of arylthallium ditrifluoroacetates (treatment with aqueous potassium iodide) (91), these latter compounds now occupy a central role in controlled biphenyl synthesis.

A further demonstration of the efficacy of photolysis of ArTlX_2 compounds is the recently described synthesis of aromatic nitriles by photolysis of solutions of arylthallium ditrifluoroacetates in aqueous potassium cyanide

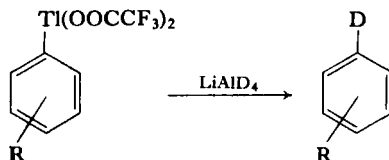
solution (147). The species present in solution is undoubtedly the complex ion $\text{ArTl}(\text{CN})_3\text{-K}^+$ (18). Photolysis presumably leads to initial homolysis of the carbon–thallium bond with the simultaneous formation of an aryl radical and thallium(II) dicyanide. The latter unstable species must disproportionate to Tl(I) [because of the high heat of formation of cyanide radicals (166), this disproportionation may involve species such as $\text{TlCN}(\text{OOCF}_3)$, leading to the formation of trifluoroacetoxy radicals; trace amounts of phenols isolated during these photolyses would be consistent with this hypothesis]. Attack on the phenyl radical by cyanide ion would give an aromatic nitrile radical anion, which by loss of an electron would give the observed aromatic nitrile. The radical process for this reaction is confirmed by observations on the photolysis of phenylthallium ditrifluoroacetate in the presence of smaller amounts of cyanide ion, which led to traces of benzene, biphenyl, several isomeric cyanobiphenyls, and (as mentioned above) phenol. Furthermore, the formation of *o*-tolunitrile from phenylacetic acid is in agreement with previous observations on the photochemically induced radical decomposition of thallium(III) phenylacetate (70).

Thiophenols may also be synthesized via the photochemical decomposition route (156). Thus, treatment of arylthallium ditrifluoroacetates with an aqueous solution of potassium *N,N*-dimethyldithiocarbamate led in quantitative yields to the formation of the corresponding aryl *N,N*-dimethyldithiocarbamates. Subsequent photolysis in aqueous acetone then led to disulfides which were reduced to the thiophenols. A small amount of aryldithiocarbamate formed as a by-product in the photolysis was converted to the same thiophenol by hydrolysis. The overall reaction sequence is illustrated in Eq. (18).



Remarkably, ArTlX_2 compounds also suffer nucleophilic substitution on the carbon–thallium bond with hydride ion to regenerate the parent arom-

atic hydrocarbon (173). The use of lithium aluminum deuteride or aluminum amalgam in D_2O thus provides a method for regiospecific introduction of deuterium into aromatic nuclei (see Scheme 7).

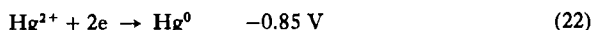
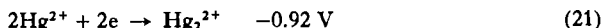
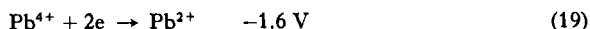


Scheme 7

The aryl-thallium bond is thus apparently capable of displacement either by electrophilic or by suitable nucleophilic reagents. Coupled with its propensity for homolytic cleavage (spontaneous in the case of $ArTlI_2$ compounds, and otherwise photochemically induced), $ArTlX_2$ compounds should be capable of reacting with a wide variety of reagents under a wide variety of conditions. Since the position of initial aromatic thallation can be controlled to a remarkable degree, the above reactions may be only representative of a remarkably versatile route to aromatic substitution reactions in which organothallium compounds play a unique and indispensable role.

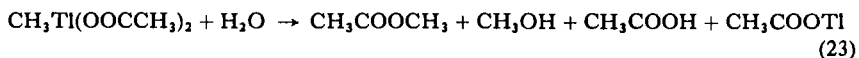
Monoalkylthallium(III) compounds can be prepared easily and rapidly by treatment of olefins with thallium(III) salts, i.e., oxythallation (66). In marked contrast to the analogous oxymercuration reaction (66), however, where treatment of olefins with mercury(II) salts results in formation of stable organomercurials, the monoalkylthallium(III) derivatives obtained from oxythallation are in the vast majority of cases spontaneously unstable, and cannot be isolated under the reaction conditions employed. Oxythallation adducts have been isolated on a number of occasions (61, 71, 104, 128), but the predominant reaction pathway which has been observed in oxythallation reactions is initial formation of an alkylthallium(III) derivative and subsequent rapid decomposition of this intermediate to give products derived by oxidation of the organic substrate and simultaneous reduction of the thallium from thallium(III) to thallium(I). The ease and rapidity with which these reactions occur have stimulated interest not only in the preparation and properties of monoalkylthallium(III) derivatives, but in the mechanism and stereochemistry of oxythallation, and in the development of specific synthetic organic transformations based on oxidation of unsaturated systems by thallium(III) salts.

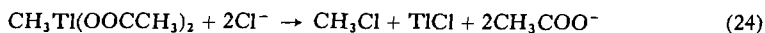
Mercury(II), thallium(III), and lead(IV) are isoelectronic and, as can be seen from the data in Eqs. (19)–(22) (77) the redox potential for thallium is intermediate between those of mercury and lead. Consequently, the relative oxidizing ability of the three metal ions should be in the order $\text{Hg(II)} <$



$\text{Tl(III)} < \text{Pb(IV)}$, and this conclusion has been confirmed recently with reference to the oxythallation of olefins (124) and the cleavage of cyclopropanes (127). It is also predictable that oxidations of unsaturated systems by Tl(III) will exhibit characteristics commonly associated with analogous oxidations by Hg(II) and Pb(IV) . There is, however, one important difference between Pb(IV) and Tl(III) redox reactions, namely that in the latter case reduction of the metal ion is believed to proceed only by a direct two-electron transfer mechanism (70). Thallium(II) has been detected by γ -irradiation (10), pulse radiolysis (17, 107), and flash photolysis (144a) studies, but is completely unstable with respect to Tl(III) and Tl(I) ; the rate constant for the process $2\text{Tl(II)} \rightarrow \text{Tl(III)} + \text{Tl(I)}$, $2.3 \times 10^9 \text{ liter mole}^{-1} \text{ sec}^{-1}$, is in fact close to diffusion control of the reaction (17).

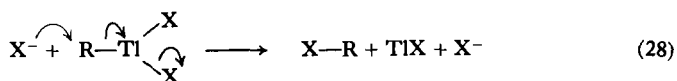
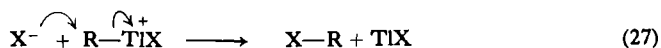
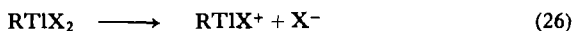
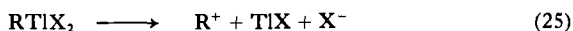
The utility of thallium(III) salts as oxidants for nonaromatic unsaturated systems is a consequence of the thermal and solvolytic instability of mono-alkylthallium(III) compounds, which in turn is apparently dependent on two major factors, namely, the nature of the associated anion and the structure of the alkyl group. Compounds in which the anion is a good bidentate ligand are moderately stable, for example, alkylthallium dicarboxylates (74, 75) or bis dithiocarbamates (76). Alkylthallium dihalides, on the other hand, are extremely unstable and generally decompose instantly. Methylthallium diacetate, for example, can readily be prepared by the exchange reaction shown in Eq. (11); it is reasonably stable in the solid state, but decomposes slowly in solution and rapidly on being heated [Eq. (23)]. Treatment with chloride ion results in the immediate formation of methyl chloride and thallium(I) chloride [Eq. (24)] (85). These facts can be accommodated on the basis that the dicarboxylates are dimeric while the



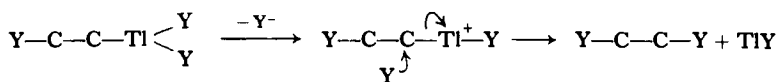
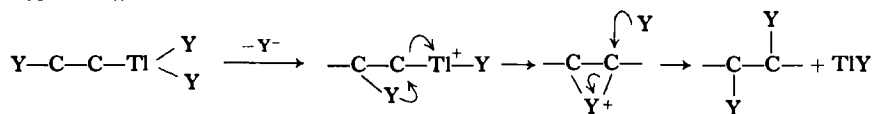
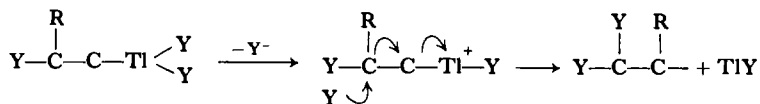
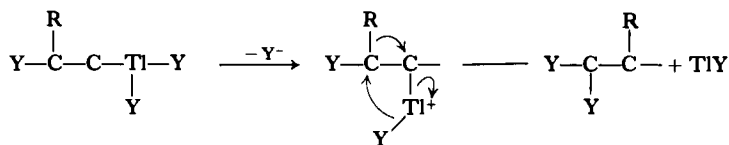
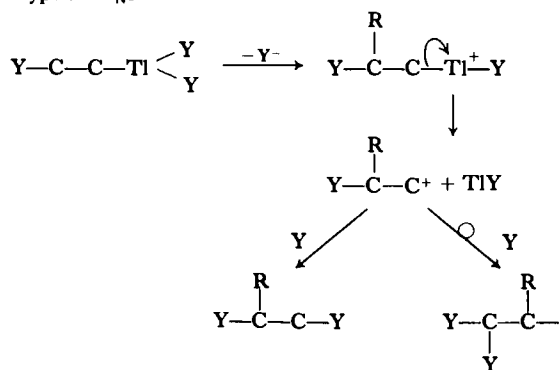


dihalides are most probably monomeric. There are unfortunately no data available as yet on the structure of the dihalides, but methylthallium diisobutyrate has been shown to be dimeric in chloroform solution, and infrared studies have indicated the presence of bridging carboxylate groups in the dimer (75).

The effect of structure of the alkyl group on the stability of monoalkylthallium(III) compounds can best be understood by reference to the different mechanisms by which these compounds undergo decomposition. A number of authors have attributed the instability of monoalkylthallium(III) compounds to facile C—Tl bond heterolysis and formation of carbonium ions [Eq. (25)] (52, 66, 79). This explanation is, however, somewhat suspect in cases where primary carbonium ions would be involved and either the two-step sequence shown in Eqs. (26), (27), or the fully synchronous $\text{S}_{\text{N}}2$ displacement shown in Eq. (28), is more compatible with the known facts. Examination of the oxythallation reactions that have been described reveals that Eq. (27) [or, for concerted reactions, Eq. (28)] can be elaborated, and that five major types of decomposition can be recognized for RTiX_2 compounds. These are outlined in Scheme 8, where Y, the nucleophile



participating in the oxythallation–dethallation sequence, may be either the anion associated with the thallium(III) salt or the solvent. In practice, Y has almost always been one of three groups, namely carboxy, hydroxy, or alkoxy. The reported stability of the neopentylthallium dihalides (60) can then be understood by reference to Scheme 8. Type 1, 2, 4, and 5 decompositions are effectively prohibited in neopentyl compounds. It is somewhat surprising that Type 3 decomposition was not observed, however, as rearrangement is frequently the predominant reaction pathway observed in solvolysis of neopentyl derivatives (145). Unlike the neopentyl case, the

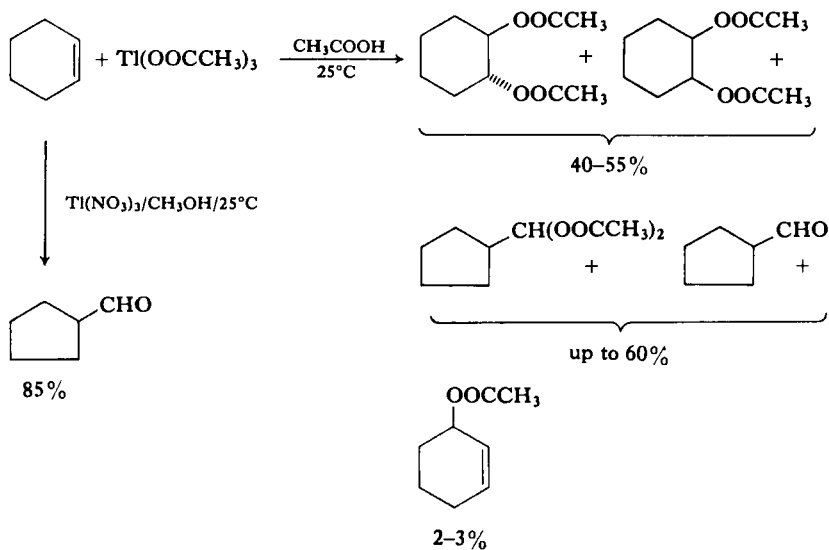
Type 1 S_N2 Type 2 S_{Ni} Type 3 S_N2 with rearrangementType 4 S_{Ni} with rearrangementType 5 S_N1 

Scheme 8

reason for the reported stability (70) of 4-pyridiomethylthallium dichloride [Eq. (13)] is less obvious.

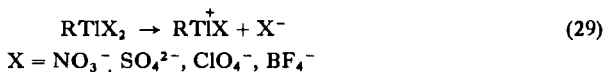
One of the most interesting aspects of the dethallation reaction is the extent (if any) to which decomposition proceeds via carbonium ions (i.e. Type 5, Scheme 8). Generation of carbonium ions (especially of the type RCH_2^+) during dethallation has been tacitly assumed by many authors; there is, however, little evidence to substantiate this assumption, and, bearing in mind that dethallation has thus far involved participation of either carboxy, hydroxy, or alkoxy groups (normally as RCOOH , H_2O , or ROH), it is obvious that the reactions can equally well be explained on the basis of Type 1–4 decompositions. There is, on the other hand, qualitative evidence that while free carbonium ions may not normally be formed in dethallation reactions, the carbon atoms carrying the thallium substituent can develop some degree of positive charge. Thus, removal of one of the anions from an RTlX_2 compound would generate the cation RTlX^+ ; due to the high electron affinity of thallium (68), it would be expected that the carbon–thallium bond in such species would be considerably weaker than in RTlX_2 compounds, and that, depending on the structure of the alkyl group, the nature of X, and the reaction conditions, substantial carbonium ion character could develop on R.

Some justification for this conclusion can be found from a comparison of the rates and products observed in the oxythallation–dethallation of olefins with different thallium(III) salts. Oxidations of olefins by thallium(III) acetate are almost infinitely slow compared to those in which the nitrate, sulfate, perchlorate, or fluoroborate salts are employed (*q.v.*). Product distribution can also vary dramatically. Thus, oxidation of cyclohexene with thallium(III) acetate in acetic acid requires several days to go to completion at room temperature and gives the mixture of products shown in Scheme 9 (3, 61, 83). Oxidation with thallium(III) nitrate in methanol, on the other hand, is complete within seconds at room temperature and gives only traces of glycol derivatives; cyclopentanecarboxaldehyde can be isolated (as its 2,4-dinitrophenylhydrazone) in 85% yield (92). Similar results have been obtained with other olefins, and these are discussed later. Two of the most important reasons for the differences observed (53) in reaction rate and product distribution with different thallium(III) salts are the relative electrophilicities of the salts themselves and the extent to which the initially formed RTlX_2 derivatives ionize by loss of an anion. Thallium(III) nitrate, sulfate, perchlorate, and fluoroborate are highly ionic reagents and the rate of oxy-



Scheme 9

thallation is predictably much faster than with the largely covalent, poorly electrophilic acetate salt. Furthermore, while NO_3^- , SO_4^{2-} , ClO_4^- , and BF_4^- are weakly chelating ligands, they are excellent leaving groups, and hence ionization as shown in Eq. (29) should be a favorable process. That is,

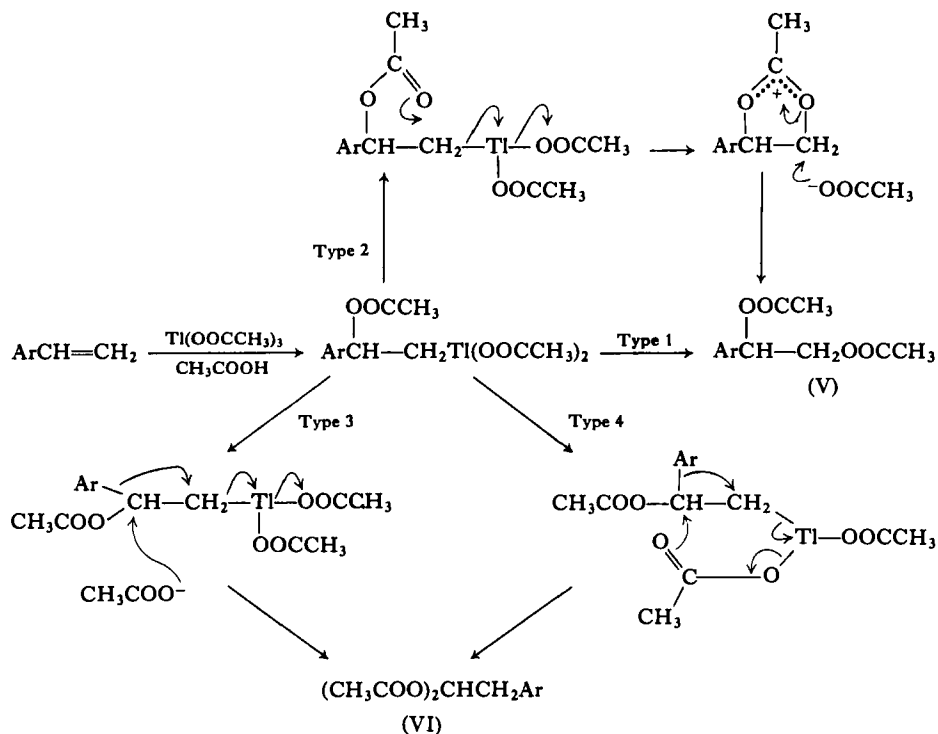


development of carbonium ion character should be pronounced in these decompositions. Acetate, on the other hand, is not an especially good leaving group but is a good bidentate ligand. Alkylthallium diacetates can thus derive a measure of stability via dimerization through acetate bridging; ionization by loss of acetate is not then particularly favorable, and hence little carbonium ion character would be expected during the decomposition of alkylthallium diacetates.

From the above discussion it follows that the probability of carbonium ion formation during decomposition of RTiX_2 compounds by a Type 5 process is low when X is carboxylate, but significantly higher when X is nitrate, sulfate, perchlorate, or fluoroborate. The important role played by the anion of the metal salt in oxymetallation has in fact been recognized only very recently for both oxymercuration (11, 12) and oxythallation (92). The

vast majority of research into oxythallation published prior to 1970 was with respect to thallium(III) acetate, and while the results of these investigations have led to some understanding of the mechanism and stereochemistry of oxythallation, few reactions of preparative significance have been discovered.

The major problem encountered in the oxidation of olefins by thallium(III) acetate is the formation of mixtures of products that are frequently

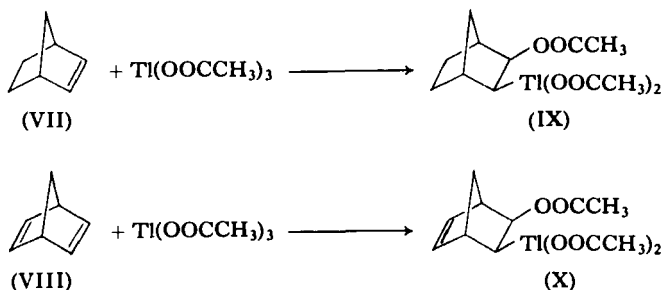


<i>Ar</i>	Product Ratio, %	
	(V)	(VI)
4-CH ₃ OC ₆ H ₄	35.7	64.3
4-CH ₃ C ₆ H ₄	74.6	25.4
3-CH ₃ C ₆ H ₄	87.6	12.4
C ₆ H ₅	92.4	7.6
4-ClC ₆ H ₄	94.2	5.8
3-ClC ₆ H ₄	98.0	2.0

Scheme 10

difficult to separate. Oxythallation of styrenes, for example, has been studied by several groups (27, 61, 124), and the products obtained in acetic acid are glycol diacetates (V) and arylacetaldehyde derivatives (VI), formation of which can readily be explained in terms of Type 1 or 2 and Type 3 or 4 decompositions, respectively (Scheme 10). From the synthetic organic chemist's point of view, conversion of styrenes to the protected aldehydes (VI) is the more interesting and useful transformation. The procedure outlined in Scheme 10 is not, however, experimentally attractive; the amount of oxidative rearrangement is acceptable only when the aromatic substituent is a very good migrating group. The situation with respect to oxidation of cycloalkenes by thallium(III) acetate is similar; oxythallation of cyclohexene, for example, gives the mixture of products shown in Scheme 9. As with the styrenes, the product of synthetic interest is that resulting from oxidative rearrangement, namely, cyclopentanecarboxaldehyde (either free or as the acetal diacetate). As a preparative procedure for these compounds, however, oxythallation with thallium(III) acetate is obviously of no significance.

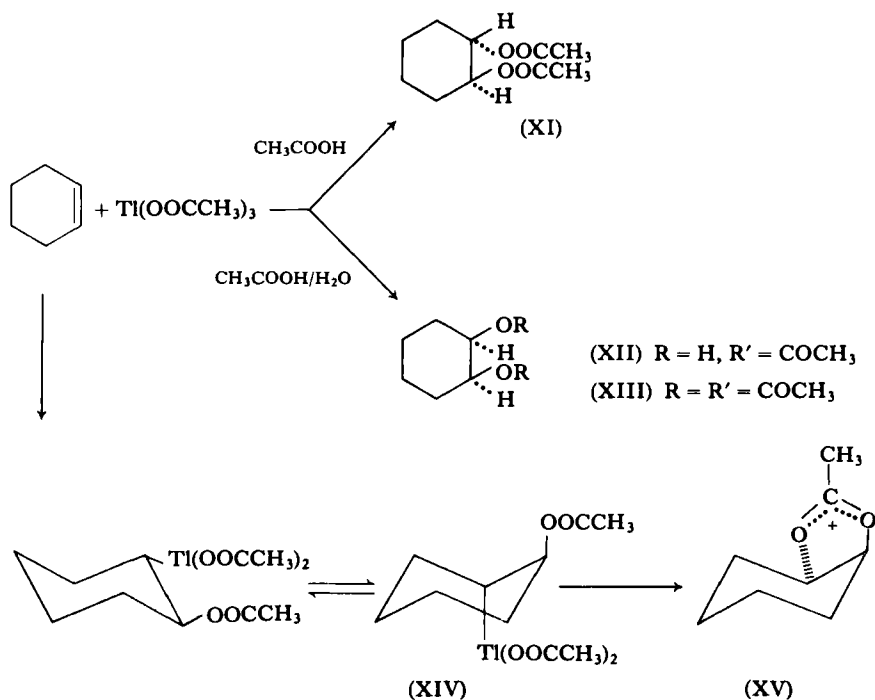
Formation of mixtures of products in these reactions can be attributed largely to the properties of the acetate group. The reactions of a number of cycloalkenes with thallium(III) salts have been investigated in some detail and the results obtained have served both to elucidate the stereochemistry of oxythallation and to underline the important role assumed by the anion of the metal salt in these oxidations. The most unambiguous evidence as to the stereochemistry of oxythallation comes from studies by Winstein on the oxythallation of norbornene (VII) and norbornadiene (VIII) with thallium(III) acetate in chloroform, in which the adducts (IX) and (X) could be precipitated from the reaction mixture by addition of pentane (128) (Scheme 11). Both by chemical means and by analogy with the oxymercuration



Scheme 11

adducts derived from (VII) and (VIII), Winstein concluded that oxythallation proceeded via *cis*-*exo* addition of the reagent. This conclusion was subsequently confirmed by Anet (4) in an elegant application of the nuclear Overhauser effect to analyses of the NMR spectra of (IX) and (X). Since oxymercuration of strained olefins such as (VII) and (VIII) is known to take place in a stereospecifically *cis* manner and oxymercuration of unstrained olefins such as cyclohexene known to occur in a stereospecifically *trans* fashion (66, 159), it was concluded that the stereochemical course of oxythallation was similar to that of oxymercuration.

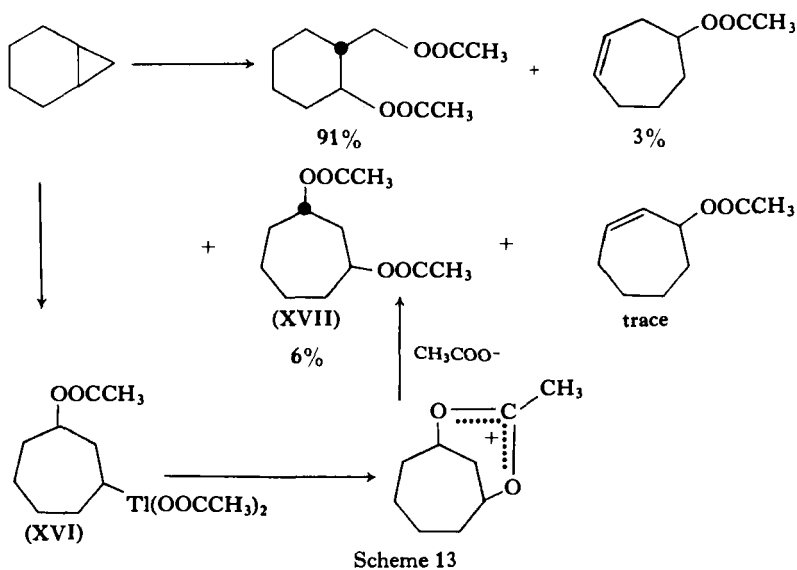
The same conclusion was drawn from the results obtained from careful studies of the stereochemistry of the glycol products formed on oxidation of cyclohexene with thallium(III) acetate (3, 83). When dry acetic acid was employed as solvent the product was mainly the *trans*-diacetate (XI); in moist acetic acid, however, the mixture of glycol mono- (XII) and diacetates (XIII) which was obtained was mainly *cis*. These results have been interpreted in terms of initial *trans* oxythallation, ring inversion,



Scheme 12

intramolecular participation of the acetoxy group in C—Tl bond heterolysis, and formation of the acetoxonium ion (XV) (Scheme 12). This is a reasonable explanation for the experimental observations, as the stereochemistry of the products obtained on solvolysis of tetramethylene-1,3-dioxolenium salts similar to (XV) is also known to undergo reversal when water is added to the solvolysis medium (170).

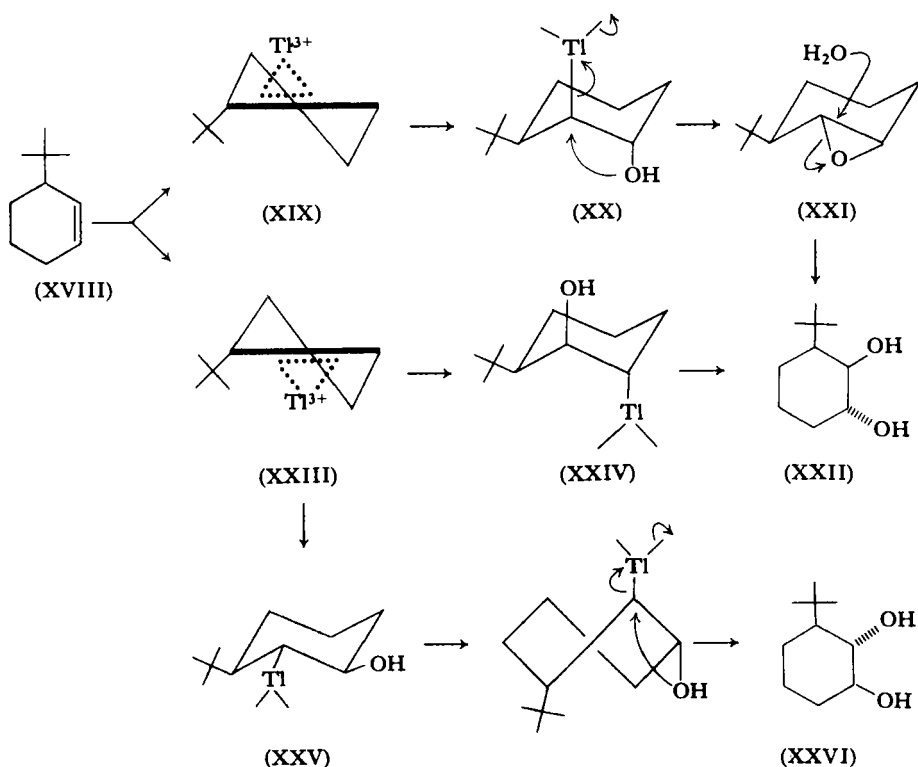
Acetoxonium ion formation has also been postulated to occur during oxidation of substituted cyclopropanes with thallium(III) acetate. These reactions are believed to proceed via the intermediacy of alkylthallium diacetates, and generally result in formation of complex mixtures of products. Oxidation of norcaradiene with thallium(III) acetate, for example, gives products derived from cleavage of both the internal and external cyclopropane bonds (Scheme 13) and production of *trans*-1,3-diacetoxycycloheptane (XVII) has been explained (125) on the basis of acetoxonium ion formation during solvolysis of the alkylthallium(III) derivative (XVI). Analogous



results have been obtained with a variety of mono- and bicyclic cyclopropanes (126, 127, 140, 143, 144), and while these reactions are of considerable mechanistic importance, they are of little synthetic utility.

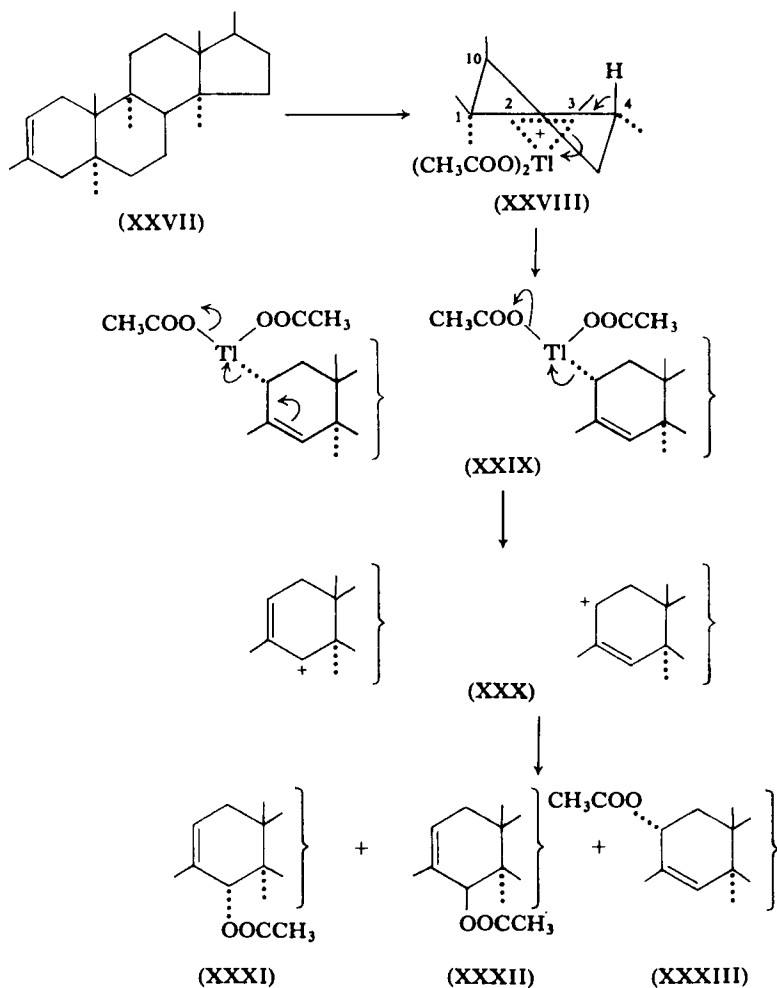
In the case of the cyclohexene adduct (XIV), the most favorable conformation should be that in which the bulky thallium substituent is equatorial;

hence ring contraction is the preferred pathway for the adduct (XIV) (83). Ring contraction would, of course, also be the preferred pathway if the initial oxythallation has taken place by cis rather than trans addition of the reagent, and the results available for cyclohexene do not omit the possibility that oxythallation may proceed partially or even largely by cis addition. Almost completely stereospecific trans addition has, however, been elegantly demonstrated by Freppel *et al.* (38). Thus, treatment of the conformationally rigid olefin (XVIII), with aqueous thallium(III) sulfate led to formation of the diols (XXII) and (XXVI) (Scheme 14) and the relative proportion of each can readily be explained. Reaction of the olefin with Tl^{3+} occurs, as expected, on the less-hindered, upper side of the molecule (with respect to the *tert*-butyl group) to give the thallinium ion (XIX). Reaction of this species with water at C-2 is effectively blocked due to the *tert*-butyl group at C-1; reaction therefore occurs at C-3 to give, exclusively, the



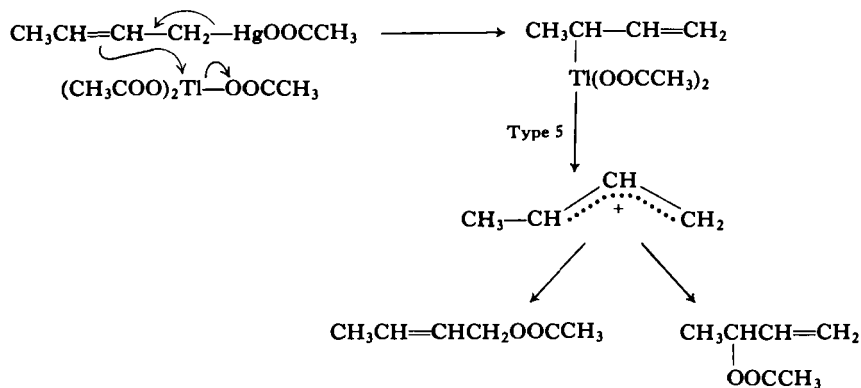
Scheme 14

trans adduct (XX). Displacement of the thallium substituent by a Type 1 process is unfavorable because of the *tert*-butyl group, and hence Type 2 reaction takes place. This probably leads to the epoxide (XXI) which undergoes acid-catalyzed ring opening to give the diol (XXII); in this case addition of the nucleophile takes place on the less sterically hindered, upper side of the molecule and gives exclusively the diol (XXII). Reaction via the *cis*-thallinium ion (XXIII) can be explained similarly, although in this instance two oxythallation adducts (XXIV) and (XXV) can be formed.



Scheme 15

Oxidation of the steroidal olefin (XXVII) with thallium(III) acetate gives mainly the allylic acetates (XXXI)–(XXXIII) (Scheme 15), again indicating that trans oxythallation is the preferred reaction course (19). Addition of the electrophile takes place from the less-hindered α -side of the molecule to give the thallinium ion (XXVIII), which by loss of a proton from C-4 would give the alkylthallium diacetate (XXIX). Decomposition of this intermediate by a Type 5 process is probably favorable, as it leads to the resonance-stabilized allylic carbonium ion (XXX), from which the observed products can be derived. Evidence in support of the decomposition process shown in Scheme 15 has been obtained from a study of the exchange reaction between *trans*-crotylmercuric acetate and thallium(III) acetate in acetic acid (Scheme 16) (142).



Scheme 16

From the evidence currently available it appears that the mechanism of oxythallation is similar to that of oxymercuration. That is, initial rapid formation of a π -complex—a "thallinium" ion—followed by rearrangement of this species to give a σ -bonded organothallium derivative (54). Decomposition of this latter intermediate by one or more of the processes shown in Scheme 8 then leads to products. The results obtained from a number of kinetic studies are in broad general agreement with this interpretation (52, 79).

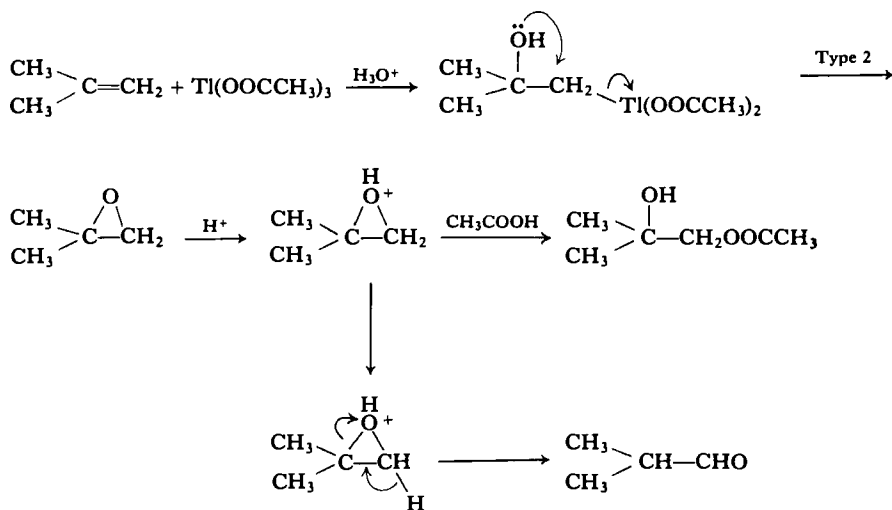
From the above discussion it is evident that adaptation of oxythallation to the development of useful synthetic transformations rests largely on the degree of control which can be exerted on the decomposition pathway of the intermediate RTlX_2 derivative. The results obtained by Freppel *et al.*, for

example, clearly indicate that in certain rigid cycloalkenes the decomposition of monoalkylthallium(III) intermediates is almost entirely limited to a Type 2 process. Control over product distribution in this work was due to stereochemical factors, but recent results by Kruse and Bednarski (71) have demonstrated that predominant Type 2 reaction can be achieved by careful control of reaction conditions. Oxidation of ethylene, propylene, and the four isomeric butenes with aqueous Tl^{3+} ion was studied originally by Henry (53, 54), and the results obtained are listed in Table VII. The distribution

TABLE VII
PRODUCTS FROM OXIDATION OF SIMPLE OLEFINS WITH Tl^{3+} /Aq.

Olefin	Carbonyl product	% Carbonyl	% Glycol
Ethylene	Acetaldehyde	45	55
Propylene	Acetone	75-85	15-25
1-Butene	Methyl ethyl ketone	45-55	15-25
<i>cis</i> -2-Butene	Methyl ethyl ketone	65-80	<0.5
<i>trans</i> -2-Butene	Methyl ethyl ketone	65-80	<0.5
Isobutene	Methyl ethyl ketone + isobutyraldehyde	35-45	55-65

of products between carbonyl and glycol derivatives was interpreted by Henry as being indicative of the relative importance of hydride or alkyl shift to direct solvolysis of the thallium substituent. As pointed out by Kruse and Bednarski, however, isobutyraldehyde can only arise from isobutene via intramolecular participation of the OH group during C—Tl bond heterolysis (i.e., Type 2 process, Scheme 17), and formation of an epoxide. This hypothesis was substantiated by the simple expedient of conducting the oxidation in weakly solvating media. Thus, oxidation of propylene with thallium(III) acetate in 50% v/v aqueous acetic acid gave a 1:1 mixture of propylene oxide and acetone. In the less polar medium 70% v/v tetrahydrofuran, 20% water, and 10% acetic acid, propylene oxide was obtained in 72% yield, together with 16% acetone and 12% 1-acetoxy-2-propanol. Using the same solvent system, oxidation of isobutene gave an epoxide-to-aldehyde ratio of 25:1. These results are particularly striking with respect to propylene; in polar, strongly solvating media, acetone is the major product (75-85%). In weakly solvating media, however, only 16% acetone is obtained. Furthermore, Kruse and Bednarski showed that epoxides served

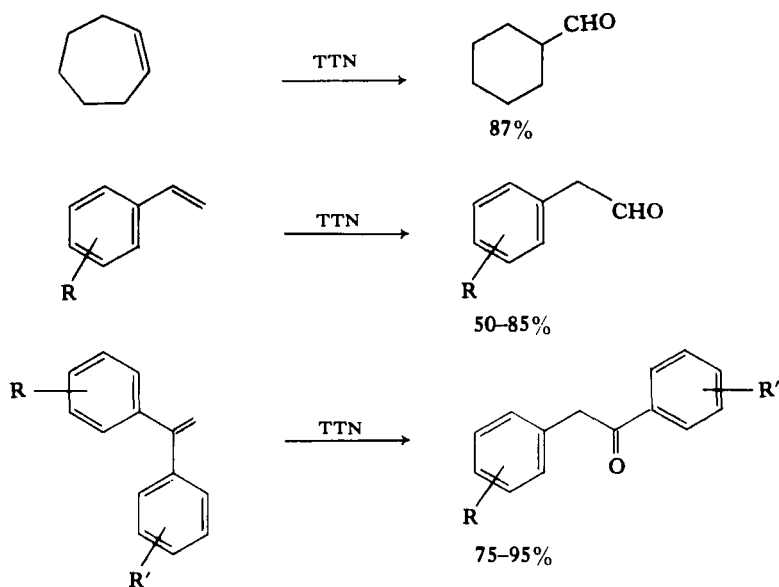


Scheme 17

as precursors only to glycol derivatives under the reaction conditions. Consequently, by appropriate control of solvent, oxythallation can be used for the conversion of olefins into either carbonyl or glycol derivatives, or into epoxides.

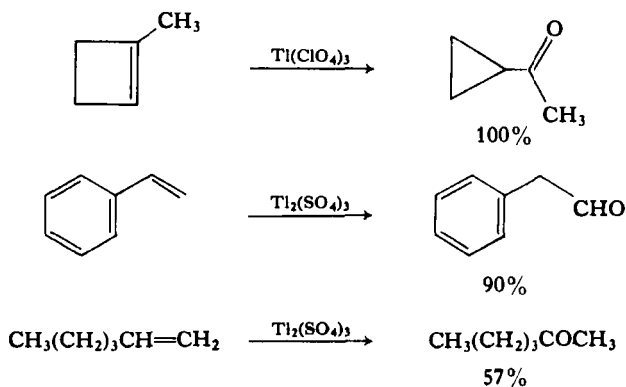
While the above examples demonstrate that product control to a significant extent is possible in oxythallation by careful choice of substrate or reaction conditions, the synthetic utility of oxythallation has been illustrated most convincingly by the results obtained with highly ionic thallium(III) salts, especially the nitrate (hereafter abbreviated TTN). Unlike the sulfate, perchlorate, or fluoroborate salts (165), TTN can easily be obtained as the stable, crystalline trihydrate which is soluble in alcohols, carboxylic acids, ethers such as dimethoxyethane (glyme), and dilute mineral acids. Oxidations by TTN can therefore be carried out under a wide variety of experimental conditions.

Examination of the reactions of a wide variety of olefins with TTN in methanol (92) has revealed that in the majority of cases oxidative rearrangement is the predominant reaction course (cf. cyclohexene, Scheme 9). Further examples are shown in Scheme 18, and the scope and limitations of this procedure for the oxidative rearrangement of various classes of simple olefins to aldehydes and ketones have been defined. From the experimental point of view these reactions are extremely simple, and most of them are



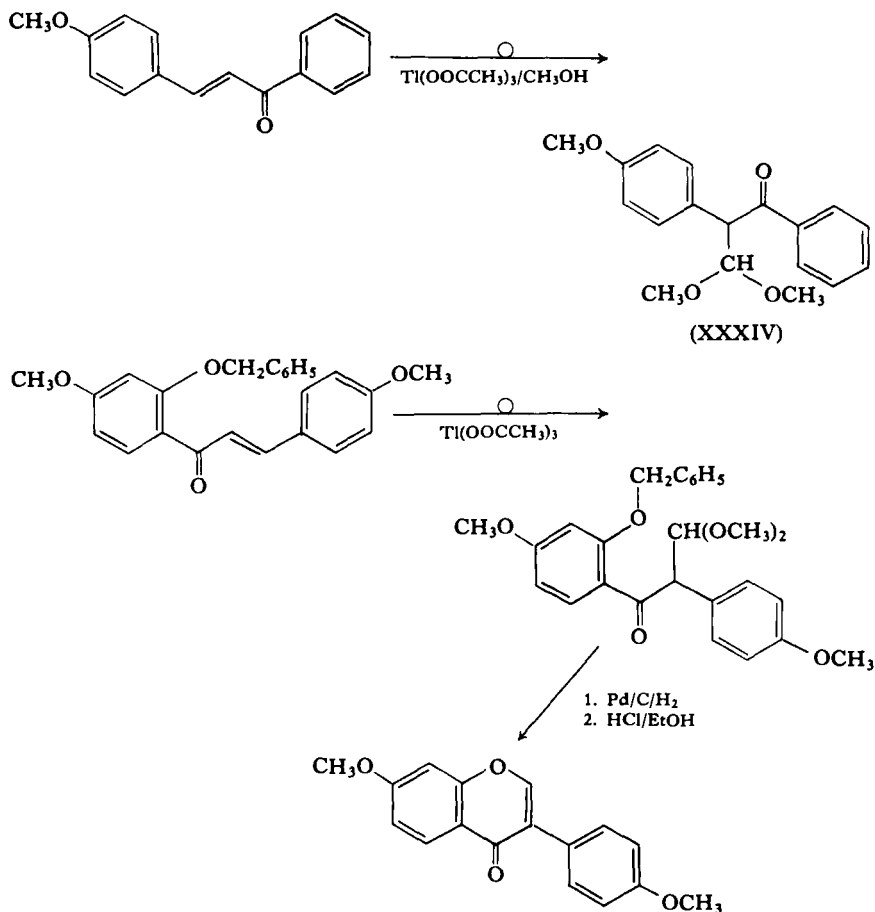
Scheme 18

complete within seconds at room temperature. Furthermore, while TTN is freely soluble in many solvents, its reduction product thallium(I) nitrate is insoluble, and hence reactions can be monitored visually. The utility of highly ionic reagents in these reactions has also been shown by Halpern *et al.* (15), who obtained cyclopropyl methyl ketone in virtually quantitative yield on treatment of 1-methylcyclobutene with thallium(III) perchlorate, and by Frye (165), who studied the oxidative rearrangement of various olefins with thallium(III) sulfate, nitrate, and fluoroborate (Scheme 19).



Scheme 19

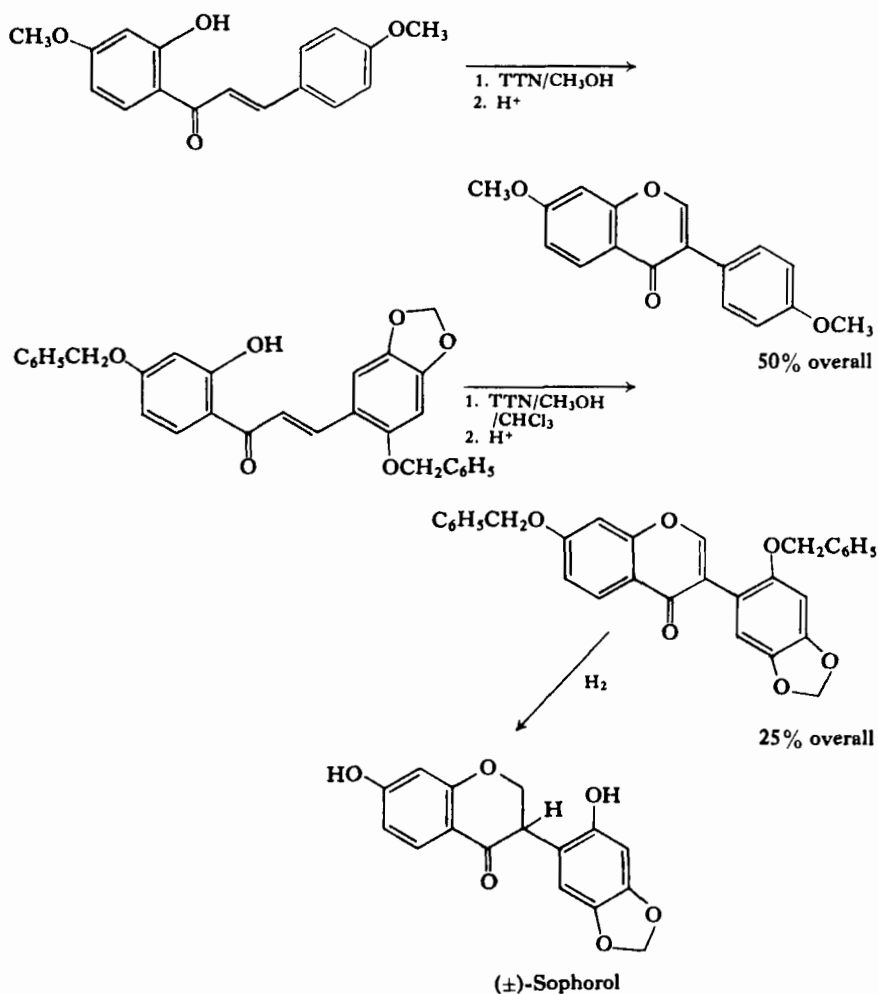
The reactions of TTN with a variety of unsaturated systems have been studied systematically during the last two years, and the results obtained clearly establish the synthetic utility of the reagent as a specific oxidant. Attempts were made in 1966 by Uemura *et al.* (162) to oxidize α,β -unsaturated carbonyl compounds with thallium(III) acetate, but were unsuccessful. In 1970, however, Ollis and his co-workers (121–123) reported that prolonged treatment of highly activated chalcones (Scheme 20) with thal-



Scheme 20

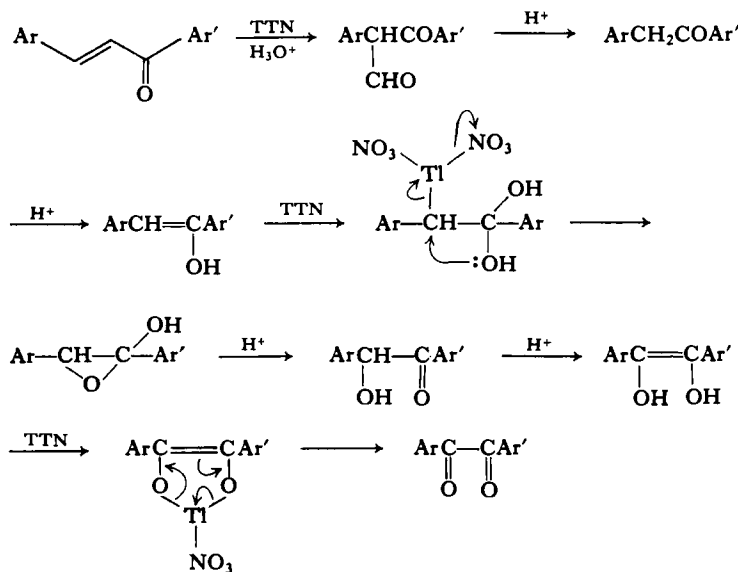
lium(III) acetate resulted in oxidative rearrangement similar to that observed with simple olefins and formation of dimethyl acetals of the type (XXXIV). When suitably substituted chalcones were used as starting material (e.g.,

Scheme 20), these acetals could readily be converted into isoflavones. Unfortunately, very low yields of rearrangement products were obtained using thallium(III) acetate, and separation and purification of acetals such as (XXXIV) was extremely tedious. Reaction of chalcones with TTN, on the other hand, is generally complete within a few hours at room temperature (95), and Farkas *et al.* (118) have developed the Ollis procedure into a simple method for the preparation of isoflavones (Scheme 21).



Scheme 21

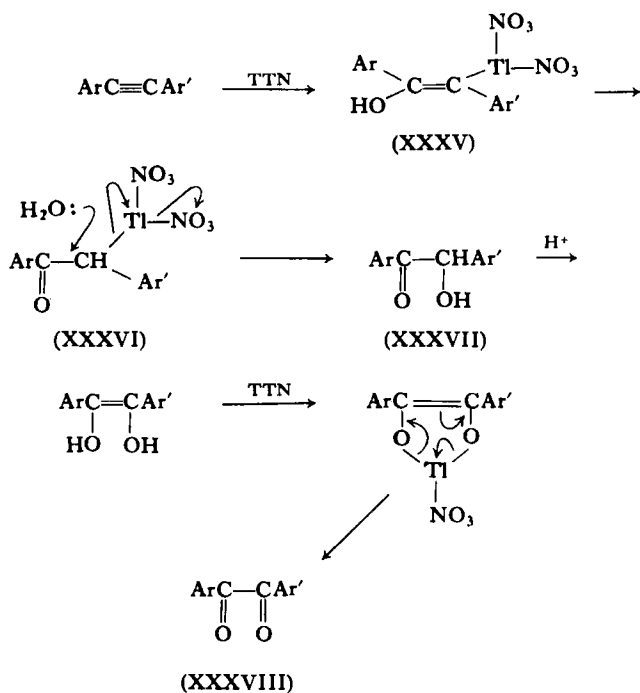
Oxidation of chalcones with TTN has been studied in detail (95, 96), and it has been shown that the products obtained depend on the amount of reagent and the solvent employed. Oxidation with 1 equivalent of TTN in methanol, methanol-chloroform, or methanol-boron trifluoride leads to acetals of the type (XXXIV) (see also Scheme 21) in yields of 20–80%. When 3 equivalents of TTN are employed, however, and aqueous glyme containing a little perchloric acid used as solvent, the products are benzils. This remarkable transformation, which proceeds in yields varying from moderate to good (40–80%), involves three distinct oxidations by TTN, and these are outlined in Scheme 22. Each individual step in this reaction sequence has been investigated in detail, with the result that useful procedures have been developed for the oxidation of both deoxybenzoins and benzoins to benzils with TTN (96).



Scheme 22

The reactions of acetylenes with thallium(III) salts are of considerable interest in that the results can be used in a qualitative comparison of reactivity between thallium(III) and mercury(II). Mercury(II) salt-catalyzed hydration of the $\text{C}\equiv\text{C}$ bond is a much studied and synthetically very useful process, although the detailed mechanism of the reaction is not known. The only published data available on the reactions of acetylenes with thallium(III) salts are due to Uemura *et al.* (161), who employed thallium(III)

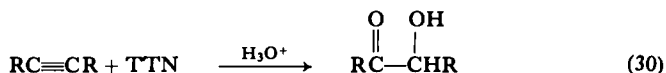
acetate and chloride as reagents. Uemura claimed that phenylacetylene could be converted into acetophenone in yields as high as 84% by treatment with thallium(III) acetate or chloride in acetic acid at 60°–110° C. This claim is, however, almost certainly specious. The reaction conditions used by the Japanese workers are incompatible with the known properties of the thallium reagents employed. Thallium(III) chloride is known to be thermally unstable with respect to thallium(I) chloride and chlorine at temperatures in excess of 40° C (141), while thallium(III) acetate has been shown to oxidize hot acetic acid rapidly and quantitatively to give thallium(I) acetoxyacetate (148). Moreover, hydration of phenylacetylene is known to occur particularly easily; it can be effected by superheated steam (31) and takes place readily at room temperature in the presence of strong acids (8, 119). Consequently, it is more than likely that Uemura and his colleagues were merely observing the acid-catalyzed hydration of phenylacetylene, and that the inorganic salts were not participating to any significant extent in the hydration process.



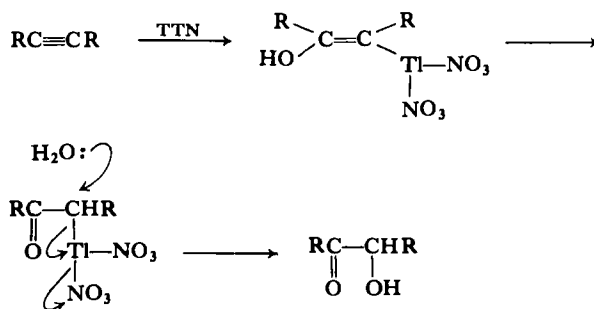
Scheme 23

These conclusions were supported by the results obtained in a study of the reactions of various types of acetylenes with TTN (94). Hydration of the $C\equiv C$ bond was found to occur to a very minor extent, if at all, with almost all of the compounds studied, and the nature of the products formed was dependent on the structure of the acetylene and the solvent employed. Oxidation of diarylacetylenes with two equivalents of TTN in either aqueous acidic glyme or methanol as solvent resulted in smooth high yield conversion into the corresponding benzils (Scheme 23). The mechanism of this oxidation in aqueous medium most probably involves oxythallation of the acetylene, ketonization of the initially formed adduct (XXXV) to give the monoalkylthallium(III) derivative (XXXVI), and conversion of this intermediate into a benzoin (XXXVII) by a Type 1 process. Oxidation of (XXXVII) to the benzil (XXXVIII) by the second equivalent of reagent would then proceed in exactly the same manner as described for the oxidation of chalcones, deoxybenzoins, and benzoins to benzils by TTN. The mechanism of oxidation in methanol solution is somewhat more complex and has not yet been fully elucidated.

Treatment of dialkylacetylenes with 1 equivalent of TTN in aqueous acidic glyme resulted in formation of acyloins in high yield [Eq. (30)]; the suggested mechanism of this transformation, shown in Scheme 24, is

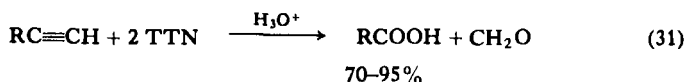


identical to that postulated for the diarylacetylenes with respect to the oxythallation–dethallation sequence. Unlike benzoins, however, acyloins show little tendency to enolize to give enediols, and hence oxidation of acyloins to α -diketones takes place only very slowly. Monoalkylacetylenes

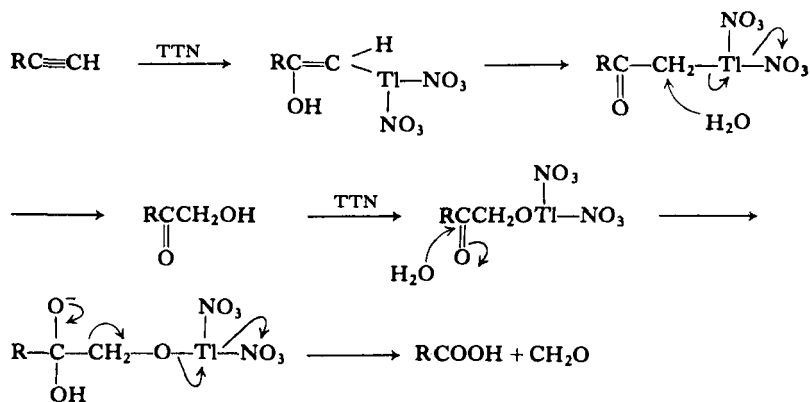


Scheme 24

were found to react exothermically with TTN; 2 equivalents of oxidant were required for completion of reaction, and the products obtained were formaldehyde and carboxylic acids containing one carbon atom less than the starting acetylene [Eq. (31)]. In these cases, oxythallation-dethallation leads to an α -keto primary alcohol, and independent experiments with

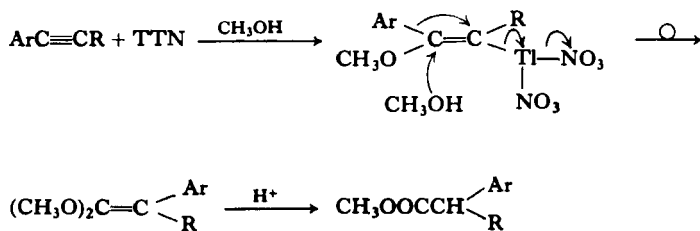


compounds containing this functional group have established that they are rapidly degraded by TTN as shown in Scheme 25. Finally, oxidation of



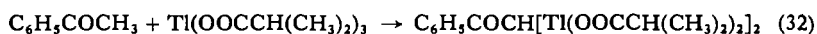
Scheme 25

alkylarylacetylenes with TTN in aqueous acidic media gave complex mixtures of products; in methanol, however, smooth oxidative rearrangement was observed, and methyl α -alkylarylacetates were produced in excellent yield. The mechanism shown in Scheme 26 has been suggested for this rearrangement (94).

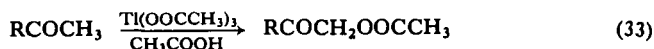


Scheme 26

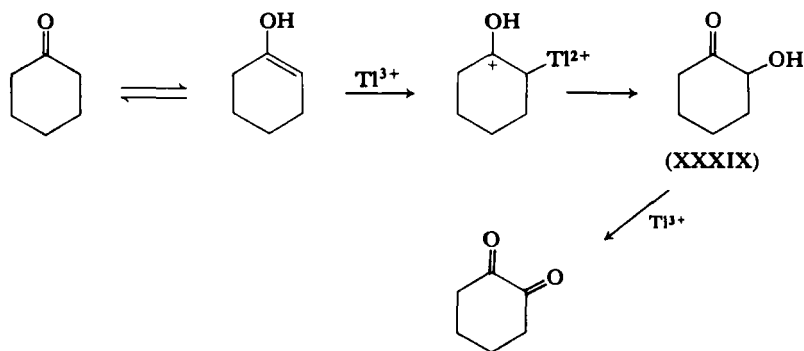
Oxidation of aldehydes and ketones with thallium(III) salts has been little investigated as yet; from the results available, however, it is evident that, as was found with olefins and acetylenes, the nature of the products obtained is largely dependent on the thallium(III) salt employed. Oxidations with thallium(III) carboxylates have been reported to give a variety of products, generally in very low yield. Thus, it has been claimed that treatment of acetaldehyde with thallium(III) salts gives glycollic aldehyde (58), but no experimental details of this work are available as yet. Treatment of acetophenone with thallium(III) isobutyrate is reported to give phenacylidene-thallium tetrakisobutyrate (49) [Eq. (32)]; reaction of both aliphatic and alicyclic ketones with thallium(III) acetate in acetic acid at elevated



temperatures, on the other hand, results in α -acetoxylation [Eq. (33)] and diacetoxylation [Eq. (34)] (6, 163).



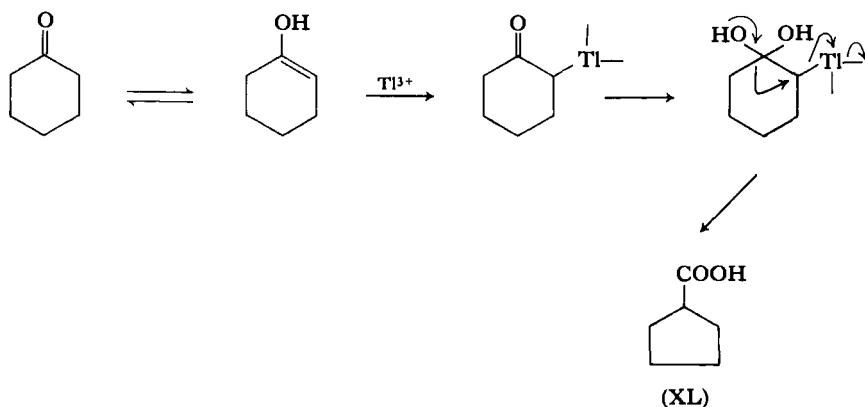
Littler has studied the oxidation of cyclohexanone with lead(IV), thallium(III), and mercury(II) salts (84), and found that with all three reagents the rates of oxidation are independent of the concentration of oxidant. Oxidation by thallium(III) and mercury(II) in 35% aqueous perchloric acid showed first-order dependence on $[\text{H}^+]$, and Littler suggested that the results were best interpreted in terms of the reaction sequence shown in Scheme 27. The major product of thallium(III) oxidation of



Scheme 27

cyclohexanone was thought to be cyclohexane-1,2-dione, which was presumed to arise via oxidation of 2-hydroxycyclohexanone (XXXIX). Oxidation of acyloins to α -diketones by thallium(III) is now known to occur very slowly, however (see above) and Littler's interpretation of the overall reaction is most probably incorrect in some of the latter details.

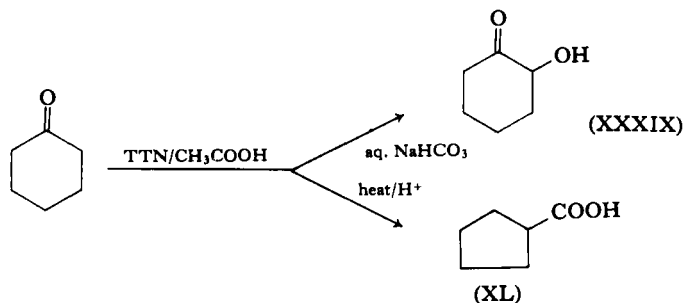
Wiberg and Koch (167) also disagreed with Littler's results, and found that the major product (75%) obtained on treatment of cyclohexanone with aqueous thallium(III) perchlorate was cyclopentanecarboxylic acid (XL). 2-Hydroxycyclohexanone was isolated in only 3% yield; unchanged starting material accounted for the remainder of the product. Wiberg and Koch were unable to detect any cyclohexane-1,2-dione in the product mixture, but did prove that 2-hydroxycyclohexanone did not function as the precursor to the ring-contracted acid. From the results obtained from a study of the oxidation of 2,2,6,6- d_4 -cyclohexanone, the mechanism shown in Scheme 28 was postulated to account for ring contraction.



Scheme 28

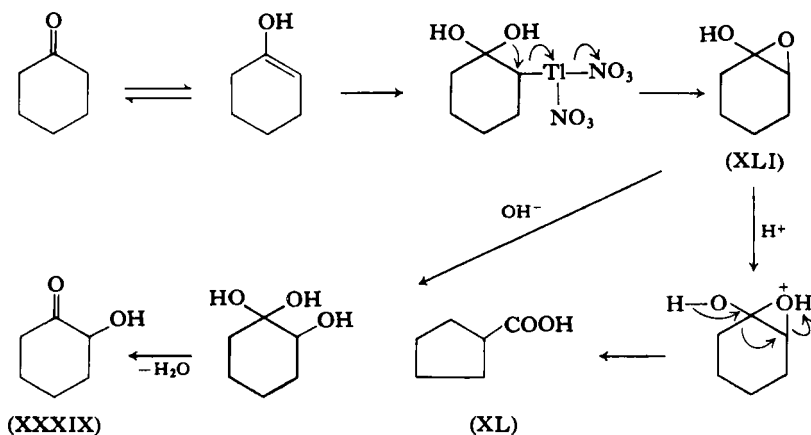
Subsequent reinvestigation of this problem using TTN in acetic acid as oxidant (93) has revealed that both Littler, and Wiberg and Koch, were partially correct, although the mechanism suggested by the latter authors for the ring contraction is certainly wrong. Addition of 1 equivalent of TTN to a solution of an equimolar amount of cyclohexanone in acetic acid results in almost instantaneous separation of 1 equivalent of thallium(I) nitrate. The nature of the oxidation product which is isolated after removal of the inorganic salt has, however, been shown to depend on the isolation technique. Thus, neutralization of the acidic medium with bicarbonate

followed by standard solvent extraction gives exclusively 2-hydroxycyclohexanone (XXXIX). Cyclopentanecarboxylic acid (XL), on the other hand, is obtained exclusively if the acidic reaction mixture is gently warmed (Scheme 29). Each product is uncontaminated by the other, and neither



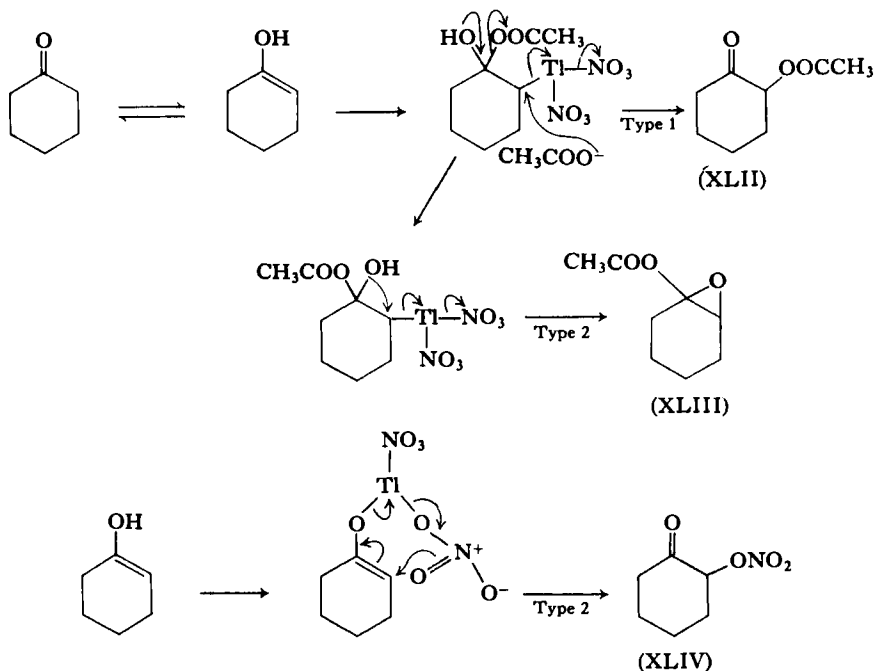
Scheme 29

can be derived from an organothallium intermediate, as all of the original thallium is removed as thallium(I) nitrate prior to isolation of the products. Furthermore, it was shown that each product is derived from a common precursor. Thus, oxidation as above and removal of thallium(I) nitrate gave an acetic acid solution which was divided into two equal portions. One of these was treated with aqueous bicarbonate and gave 2-hydroxycyclohexanone. The other was heated for a few minutes and gave cyclopentanecarboxylic acid. These results have been explained in terms of the reactions shown in Scheme 30; that is, the epoxenol (XLI) serves as the common



Scheme 30

precursor to both (XXXIX) and (XL). The mechanism shown in Scheme 30 is, moreover, consistent with the observations that none of the esters (XLII)–(XLIV) is the immediate precursor. Plausible mechanisms can be postulated both for formation of these intermediates (Scheme 31) and for

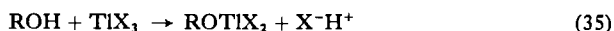


Scheme 31

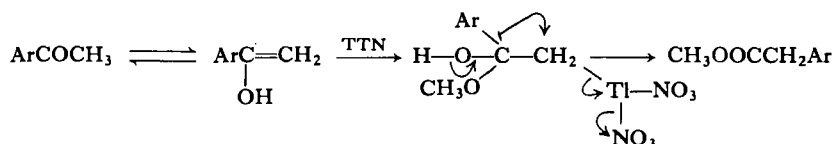
their subsequent conversion into (XXXIX) and (XL). Each of the esters (XLII)–(XLIV) was prepared independently and subjected to the isolation procedures used in the oxidation reaction. Both (XLII) and (XLIV) were recovered virtually unchanged from aqueous sodium bicarbonate solution and hot acetic acid. Treatment of (XLIII) with aqueous sodium bicarbonate solution resulted in quantitative hydrolysis to (XXXIX), but all attempts to induce ring contraction of (XLIII) to (XL) were unsuccessful.

One of the most interesting features of the above discussion is that the experimental observations can be readily explained on the basis of oxythallation of the enolic $\text{C}=\text{C}$ bond (Scheme 30), but not by a process involving formation of an O-Ti bond (Scheme 31). Facile ligand exchange of the type shown in Eq. (35) has been observed with alcohols, phenols, carboxylic

acids, and oximes; with simple enols, however, oxythallation is apparently



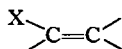
the more rapid reaction. Supporting evidence for this conclusion has been obtained from a study of the oxidation of acetophenones with TTN in acidic methanol (97). Treatment of a variety of acetophenones with TTN in acidic methanol at room temperature resulted in smooth oxidative rearrangement and formation of methyl arylacetates in yields varying from moderate to excellent (45–90%). This simple procedure in fact constitutes the method of choice in many cases for the preparation of this important class of synthetic intermediates. The mechanism proposed for this rearrangement is shown in Scheme 32 (cf. the Wiberg–Koch mechanism shown in Scheme 28), and isotopic labeling techniques have been employed to prove that reaction proceeds via 1,2-aryl migration. As in the oxidation of styrenes by thallium(III) salts (Scheme 10), both the rate of oxidation of acetophenones and the extent to which rearrangement occurs to give methyl



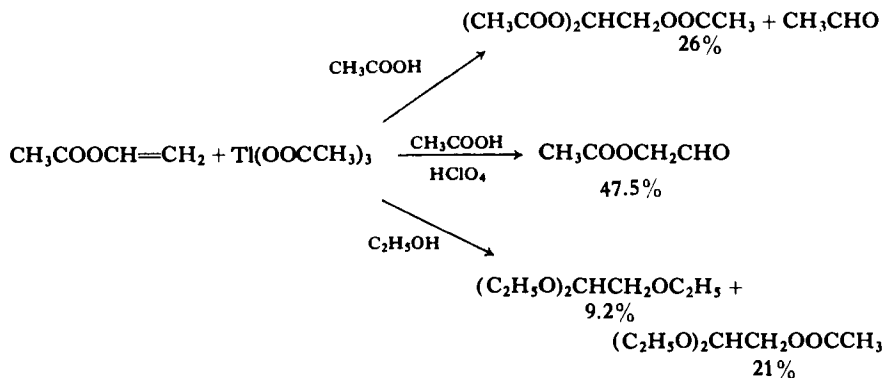
Scheme 32

arylacetates are dependent to a major extent on the relative migratory aptitudes of the aromatic substituents. This synthesis is thus most useful when the aromatic substituent contains electron-donating substituents.

Enolized carbonyl compounds can be regarded as belonging to the general class of olefins

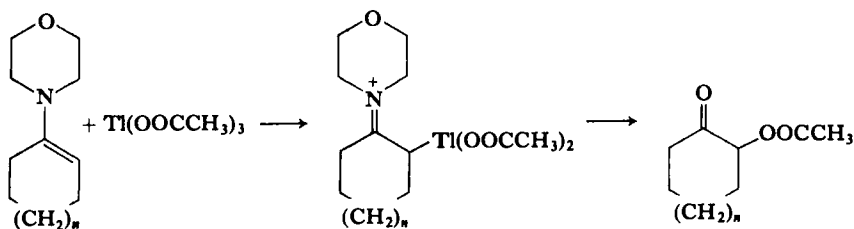


where X = O, S, N, halogen, etc. The reactions of such olefins with thallium(III) salts have not yet been investigated systematically, and from the evidence available there is no clear pattern of reactivity. Uemura *et al.* studied the reactions of vinyl acetate with thallium(III) acetate (162). The products obtained, mostly in low yields, varied with reaction conditions (Scheme 33), and these oxidations are of little preparative significance. Oxidation of enamines with thallium(III) acetate under carefully controlled



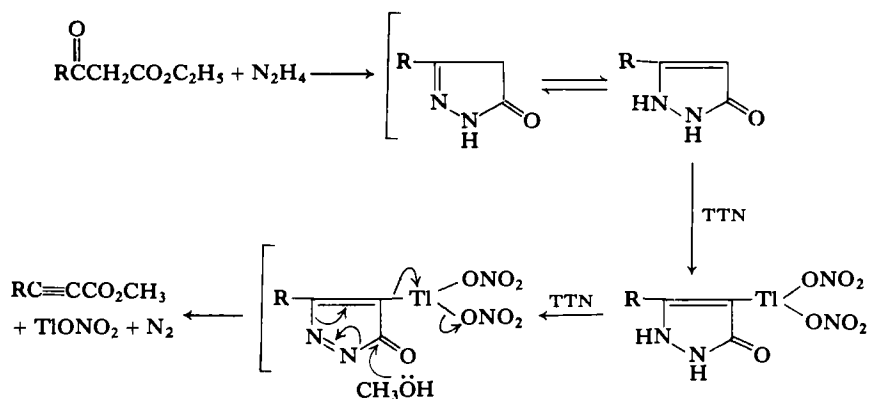
Scheme 33

conditions has, however, been shown to lead to good yields of α -acetoxyketones (72) (Scheme 34).



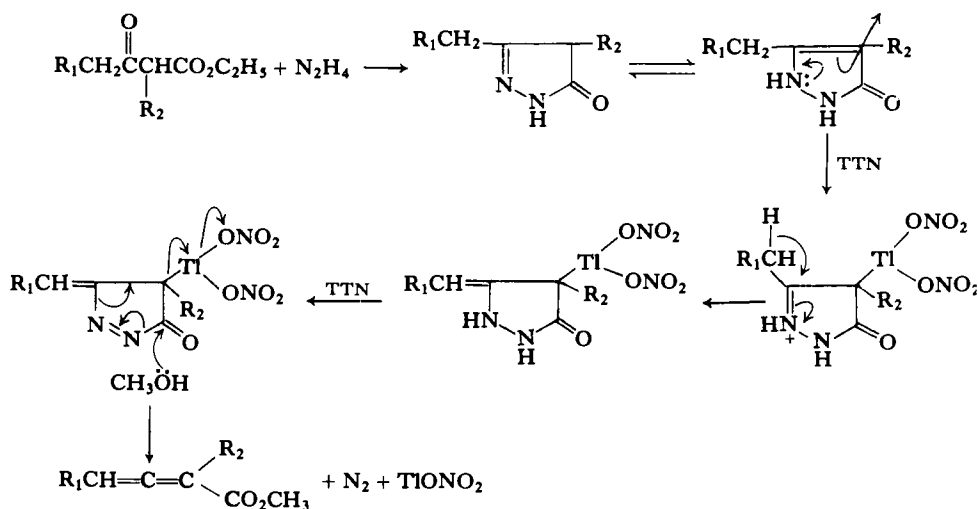
Scheme 34

The recently reported (157) conversion of 5-pyrazolones directly to α,β -acetylenic esters by treatment with TTN in methanol appears to be an example of thallation of a heterocyclic enamine; the suggested mechanism involves initial electrophilic thallation of the 3-pyrazolin-5-one tautomer of the 5-pyrazolone to give an intermediate organothallium compound which undergoes a subsequent oxidation by a second equivalent of TTN to give a diazacyclopentadienone. Solvolysis by methanol, with concomitant elimination of nitrogen and thallium(I), yields the α,β -acetylenic ester in excellent (78–95%) yield (Scheme 35). Since 5-pyrazolones may be prepared in quantitative yield by the reaction of β -keto esters with hydrazine (168), this conversion represents in a formal sense the dehydration of β -keto esters. In fact, the direct conversion of β -keto esters to α,β -acetylenic esters without isolation of the intermediate 5-pyrazolones can be achieved by treatment in methanol solution first with hydrazine and then with TTN.



Scheme 35

Under the same reaction conditions, β -keto esters which have been alkylated on the α -carbon atom (thus leading to 3,4-disubstituted 5-pyrazolones upon treatment with hydrazine) give *allenic esters* in good (50–70%) yield (158). The mechanism (Scheme 36) again appears to involve thallation of the enamine tautomer of the 5-pyrazolone, but deprotonation now takes place



Scheme 36

from the 3-substituent rather than from the 4-position (which is now blocked by an alkyl substituent; compare with Scheme 35), and subsequent oxidation of the cyclic hydrazone followed by methanolysis leads directly to an allenic

ester. The ready availability of alkylated β -keto esters (151) and their facile conversion to pyrazolones (168) make this route to allenes particularly appealing.

REFERENCES

1. Ahrland, S., Chatt, J., and Davies, N. R., *Quart. Rev. (London)* **12**, 265 (1958).
2. Altland, H. W., Ph.D. Thesis, Princeton Univ., New Jersey, 1971.
3. Anderson, C. B., and Winstein, S., *J. Org. Chem.* **28**, 605 (1963).
4. Anet, F. A. L., *Tetrahedron Lett.* 3399 (1964).
5. Belgian Patent 620663 (1962); *Chem. Abstr.* **59**, 10120 (1963).
6. Birch, S. F., *J. Chem. Soc.* 1132 (1934).
7. Bock, R., and Monerjan, A., *Fresenius Z. Anal. Chem.* **235**, 317 (1968).
8. Bott, R. W., Eaborn, C., and Walton, D. R. M., *J. Chem. Soc.* 384 (1965).
9. Bowden, K., and Cockerill, A. F., *Chem. Commun.* 989 (1967).
10. Brown, D. M., and Dainton, F. S., *Trans. Faraday Soc.* **62**, 1139 (1966).
11. Brown, H. C., and Kurek, J. T., *J. Amer. Chem. Soc.* **91**, 5647 (1969).
12. Brown, H. C., and Rei, M.-H., *J. Amer. Chem. Soc.* **91**, 5646 (1969).
13. Brown, H. C., and Wirkkala, R. A., *J. Amer. Chem. Soc.* **88**, 1447, 1453, 1456 (1966).
14. Bruce, M. I., *Org. Mass Spectrom.* **2**, 1037 (1969).
15. Byrd, J. E., Cassar, L., Eaton, P. E., and Halpern, J., *Chem. Commun.* 40 (1971).
16. Calderon, J. L., Cotton, F. A., and Legzdins, P., *J. Amer. Chem. Soc.* **91**, 2528 (1969).
17. Cercek, B., Ebert, M., and Swallow, A. J., *J. Chem. Soc., A* 612 (1966).
18. Challenger, F., and Richards, O. V., *J. Chem. Soc.* 405 (1934).
19. Cocton, B., and Paulet de, A. C., *Bull. Soc. Chim. Fr.* 2947 (1966).
20. Coombes, R. G., Johnson, M. D., and Vamplew, D., *J. Chem. Soc., A* 2297 (1968).
21. Cooper, R., Fischer, E. O., and Semmlinger, W., *J. Organometal. Chem.* **9**, 333 (1967).
22. Corey, E. J., Koelliker, U., and Neuffer, J., *J. Amer. Chem. Soc.* **93**, 1489 (1971).
23. Corey, E. J., Ravindranathan, T., and Terashima, S., *J. Amer. Chem. Soc.* **93**, 4326 (1971).
24. Cotton, F. A., and Legzdins, P., *J. Amer. Chem. Soc.* **90**, 6232 (1968).
25. Cotton, F. A., and Reynolds, L. T., *J. Amer. Chem. Soc.* **80**, 269 (1958).
26. Cotton, F. A., and Wilkinson, G., "Advanced Inorganic Chemistry," p. 440. Wiley (Interscience), New York, 1966; see also Lee (79), pp. 73-75.
27. Criegee, R., *Angew. Chem.* **70**, 173 (1958).
28. Criegee, R., Dimroth, P., and Schempf, R., *Chem. Ber.* **90**, 1337 (1957).
29. Davidson, J. M., and Triggs, C., *J. Chem. Soc., A* 1324 (1968).
30. Deacon, G. B., and Parrott, J. C., *J. Organometal. Chem.* **15**, 11 (1968).
31. Desgrez, A., *Ann. Chim. (Paris)* **3**, 231 (1894).
32. Faraglia, G., Fiorani, L. R., Repe, B. C. L., and Barbieri, R., *Inorg. Nucl. Chem. Lett.* **2**, 277 (1966).
33. Fear, C. M., and Menzies, E. M., *J. Chem. Soc.* 937 (1926).
34. Fischer, E. O., *Angew. Chem.* **69**, 207 (1957).
35. Fischer, E. O., and Fritz, H. P., *Advan. Inorg. Chem. Radiochem.* **1**, 56 (1959).
36. Fischer, E. O., and Piesbergen, U., *Z. Naturforsch. B* **11**, 758 (1956).
37. Frasson, E., Meneus, F., and Panattoni, C., *Nature (London)* **199**, 1087 (1963).
38. Freppel, C., Favier, R., Richer, J.-C., and Zador, M., *Can. J. Chem.* **49**, 2586 (1971).
39. Fritz, H. P., *Advan. Organometal. Chem.* **1**, 239 (1964).

40. Fritz, H. P., and Schneider, R., *Chem. Ber.* **93**, 1171 (1960).
41. Gavrilova, L. D., and Zhdanov, S. I., *Collect. Czech. Chem. Commun.* **32**, 2215 (1967).
42. Gilman, H., and Abbott, R. K., Jr., *J. Amer. Chem. Soc.* **65**, 122 (1943).
43. Gilman, H., and Jones, R. G., *J. Amer. Chem. Soc.* **68**, 517 (1946).
44. Gilman, H., and Jones, R. G., *J. Amer. Chem. Soc.* **72**, 1760 (1950).
45. Gilman, H., and Jones, R. G., *J. Amer. Chem. Soc.* **62**, 2357 (1940).
46. Glushkova, V. P., and Kocheshkov, K. A., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 1391 (1957).
47. Glushkova, V. P., and Kocheshkov, K. A., *Dokl. Akad. Nauk SSSR*, **116**, 233 (1957).
48. Glushkova, V. P., and Kocheshkov, K. A., *Dokl. Akad. Nauk. SSSR*, **103**, 615 (1955).
49. Glushkova, V. P., and Kocheshkov, K. A., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 1186 (1957).
50. Groll, H. P. A., *J. Amer. Chem. Soc.* **52**, 2998 (1930).
51. Hart, C. R., and Ingold, C. K., *J. Chem. Soc.* 4372 (1964).
52. Henry, P. M., *Advan. Chem. Ser.* **70**, 126 (1968).
53. Henry, P. M., *J. Amer. Chem. Soc.* **87**, 4423 (1965).
54. Henry, P. M., *J. Amer. Chem. Soc.* **87**, 990 (1965).
- 54a. Heyman, D. A., *J. Organometal. Chem.* **35**, C57 (1972).
55. Hull, H., and Turnbull, A. G., *Inorg. Chem.* **6**, 2020 (1967).
56. Hunt, C. C., and Doyle, J. R., *Inorg. Chem. Nucl. Lett.* **2**, 283 (1966).
57. Jacko, M. G., and Price, S. J. W., *Can. J. Chem.* **43**, 1961 (1965).
58. Japanese Patent, 69 11, 887 (1969); *Chem. Abstr.* **71**, 112 416 (1969).
59. Johnson, B. F. G., Lewis, T., and White, D. A., *J. Amer. Chem. Soc.* **91**, 5186 (1969).
60. Johnson, M. D., *Chem. Commun.* 1037 (1970).
61. Kabbe, H.-J., *Justus Liebigs Ann. Chem.* **656**, 204 (1962).
62. Katz, T. L., and Mrowca, J. J., *J. Amer. Chem. Soc.* **89**, 1105 (1967).
63. Kharasch, M. S., and Isbell, H. S., *J. Amer. Chem. Soc.* **53**, 3053 (1932).
64. King, R. B., *Inorg. Chem.* **7**, 90 (1968).
65. King, R. B., Kapoor, R. N., and Pannell, K. H., *J. Organometal. Chem.* **20**, 187 (1969).
66. Kitching, W., *Organometal. Chem. Rev., Sect. A* **3**, 61 (1968).
67. Kitching, W., *Organometal. Chem. Rev., Sect. A* **3**, 35 (1968).
68. Kitching, W., *Rev. Pure Appl. Chem.* **19**, 1 (1969).
69. Klopman, G., *J. Amer. Chem. Soc.* **90**, 223 (1968).
70. For discussion and leading references, see Kochi, J. K., and Bethea, T. W., III, *J. Org. Chem.* **33**, 75 (1968).
71. Kruse, W., and Bednarski, T. M., *J. Org. Chem.* **36**, 1154 (1971).
72. Kuehne, M. E., and Giacobbe, T. J., *J. Org. Chem.* **33**, 3359 (1968).
73. Kurosawa, H., and Okawara, R., *Organometal. Chem. Rev., Sect. A* **6**, 65 (1970).
74. Kurosawa, H., and Okawara, R., *Inorg. Nucl. Chem. Lett.* **3**, 93 (1967).
75. Kurosawa, H., and Okawara, R., *J. Organometal. Chem.* **10**, 211 (1967).
76. Kurosawa, H., and Okawara, R., *J. Organometal. Chem.* **14**, 225 (1968).
77. Latimer, W., "Oxidation Potentials," 2nd ed. Prentice-Hall, Englewood Cliffs, New Jersey, 1961.
78. Lee, A. G., *Quart. Rev. (London)* **24**, 310 (1970).
79. Lee, A. G., "The Chemistry of Thallium." Elsevier, Amsterdam, 1971.
80. Lee, A. G., *Chem. Commun.* 1614 (1968).
81. Lee, A. G., *J. Organometal. Chem.* **22**, 537 (1970).
82. See, e.g., Lee, A. G., and Sheldrick, G. M., *J. Organometal. Chem.* **17**, 481 (1969).
83. Lee, J. B., and Price, M. J., *Tetrahedron* **20**, 1017 (1964).

84. Littler, J. S., *J. Chem. Soc.* 827 (1962).
85. Lodochnikova, V. I., Panov, E. M., and Kocheshkov, K. A., *Zh. Obshch. Khim.* **33**, 1199 (1963).
86. McKillop, A., Elsom, L. F., and Taylor, E. C., *J. Organometal. Chem.* **15**, 500 (1968).
87. McKillop, A., Elsom, L. F., and Taylor, E. C., *J. Amer. Chem. Soc.* **90**, 2423 (1968).
88. McKillop, A., Elsom, L. F., and Taylor, E. C., *Tetrahedron* **26**, 4041 (1970).
89. McKillop, A., Fowler, J. S., Zelesko, M. J., Hunt, J. D., and Taylor, E. C., *Tetrahedron Lett.* 2423 (1969).
90. McKillop, A., Hunt, J. D., and Taylor, E. C., *J. Organometal. Chem.* **24**, 77 (1970).
91. McKillop, A., Hunt, J. D., Zelesko, M. J., Fowler, J. S., Taylor, E. C., McGillivray, G., and Kienzle, F., *J. Amer. Chem. Soc.* **93**, 4841 (1971).
92. McKillop, A., Hunt, J. D., Taylor, E. C., and Kienzle, F., *Tetrahedron Lett.* 5275 (1970).
93. McKillop, A., Hunt, J. D., and Taylor, E. C., *J. Org. Chem.* in press.
94. McKillop, A., Oldenzil, O. H., Swann, B. P., Taylor, E. C., and Robey, R. L., *J. Amer. Chem. Soc.* **93**, 7331 (1971).
95. McKillop, A., Swann, B. P., and Taylor, E. C., *Tetrahedron Lett.* 5281 (1970).
96. McKillop, A., Swann, B. P., Ford, M. E., and Taylor, E. C., *J. Amer. Chem. Soc.* in press.
97. McKillop, A., Swann, B. P., and Taylor, E. C., *J. Amer. Chem. Soc.* **93**, 4919 (1971).
98. Maher, J. P., and Evans, D. F., *J. Chem. Soc.* 5534 (1963).
99. Maher, J. P., and Evans, D. F., *J. Chem. Soc.* 637 (1965).
100. For a recent review, see Maitlis, P. M., "The Organic Chemistry of Palladium," Vol. II. Academic Press, New York, 1971.
101. Meister, H., East German Patent 942989 (1956); *Chem. Abstr.* **52**, 16249 (1958).
102. Meister, H., *Angew. Chem.* **69**, 533 (1957).
103. Menzies, R. C., and Wilkins, E. M., *J. Chem. Soc.* 1148 (1924).
104. Menzies, R. C., and Cope, I. S., *J. Chem. Soc.* 2862 (1932).
105. Mrowca, J. J., Ph.D. Thesis, Columbia Univ., New York, 1966.
106. Müller, J., and Dehnicke, K., *J. Organometal. Chem.* **12**, 37 (1968).
107. Muller, J.-C., Ferradini, C., and Pucheault, J., *J. Chim. Phys.* **63**, 232 (1966).
108. Nesmeyanov, A. N., Anisimov, K. N., and Kolobova, N. E., *Izv. Akad. Nauk SSSR, Ser. Khim.* 2220 (1964).
109. Nesmeyanov, A. N., Anisimov, K. N., Kolobova, N. E., and Baryshnikov, L. I., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 193 (1963).
110. Nesmeyanov, A. N., Dvoryantseva, G. A., Kochetkova, N. S., Materikova, R. B., and Sheinker, Y. N., *Dokl. Akad. Nauk SSSR* **159**, 847 (1964).
111. Nesmeyanov, A. N., and Kocheshkov, K. A., "Methods of Elemento-Organic Chemistry," Vol. 4. North-Holland Publ., Amsterdam, 1967.
112. Nesmeyanov, A. N., Kochetkova, N. S., and Materikova, R. B., *Dokl. Akad. Nauk SSSR*, **147**, 113 (1962).
113. Nesmeyanov, A. N., Materikova, R. B., Brainina, E. M., and Kochetkova, N. S., *Izv. Akad. Nauk SSSR, Ser. Khim.* 1323 (1969).
114. Nesmeyanov, A. N., Materikova, R. B., Fedin, E. I., Kochetkova, N. S., Petrovskii, P. V., Fedorov, L. A., and Leonov, E. V., *Dokl. Akad. Nauk SSSR* **177**, 586 (1967).
115. Nesmeyanov, A. N., Materikova, R. B., and Kochetkova, N. S., *Izv. Akad. Nauk SSSR* 1334 (1963).
116. Nesmeyanov, A. N., Materikova, R. B., Kochetkova, N. S., and Luk'yanova, R. V., *Izv. Akad. Nauk SSSR Ser. Khim.* 975 (1969).
117. Nesmeyanov, A. N., Materikova, R. B., Kochetkova, N. S., and Leonova, E. V., *Dokl. Akad. Nauk SSSR* **177**, 131 (1967).

118. Farkas, L., Gottsegen, A., Nógrádi, M., and Antus, S. *J. Chem. Soc., Chem. Commun.* 825 (1972).
119. Noyce, D. S., and Schiavelli, M. D., *J. Amer. Chem. Soc.* **90**, 1020, 1023 (1968).
120. Okhlobystin, O. Yu., Bilevitch, K. A., and Zakharkin, L. I., *J. Organometal. Chem.* **2**, 281 (1964).
121. Ollis, W. D., Ormand, K. L., and Sutherland, I. O., *Chem. Commun.* 1237 (1968).
122. Ollis, W. D., Ormand, K. L., and Sutherland, I. O., *J. Chem. Soc., C* 119 (1970).
123. Ollis, W. D., Ormand, K. L., Redman, B. T., Roberts, R. D., and Sutherland, I. O., *J. Chem. Soc., C* 125 (1970).
124. Ouellette, R. J., Kordosky, G., Levin, C., and Williams, S., *J. Org. Chem.* **34**, 4104 (1969).
125. Ouellette, R. J., Shaw, D. L., and South, A., Jr., *J. Amer. Chem. Soc.* **86**, 2744 (1964).
126. Ouellette, R. J., South, A., Jr., and Shaw, D. L., *J. Amer. Chem. Soc.* **87**, 2602 (1965).
127. Ouellette, R. J., and Williams, S., *J. Org. Chem.* **35**, 3210 (1970).
128. Pande, K. C., and Winstein, S., *Tetrahedron Lett.* 3393 (1964).
129. Panov, E. M., and Kocheshkov, K. A., *Dokl. Akad. Nauk. SSSR* **85**, 1037 (1952).
130. Pearson, R. G., *Surv. Progr. Chem.* **5**, 1 (1969).
131. Pearson, R. G., *Science* **151**, 172 (1966).
132. Pohlmann, J. L. W., and Brinckmann, F. E., *Z. Naturforsch., B* **20**, 5 (1965).
133. Reuss, F. R., and Janßen, J., *Arch. Pharm. (Weinheim)* **295**, 284 (1962).
134. Reutov, O. A., and Beletskaya, I. P., "Reaction Mechanisms of Organometallic Compounds," pp. 215-219. North-Holland Publ., Amsterdam, 1968.
135. Reynolds, L. T., and Wilkinson, G., *J. Inorg. Nucl. Chem.* **9**, 86 (1959).
136. Rochow, E. G., and Dennis, L. M., *J. Amer. Chem. Soc.* **57**, 486 (1935).
137. Rosenblum, M., "Chemistry of the Iron Group Metallocenes." Wiley, New York, 1965.
138. Sheldrick, G. M., and Sheldrick, W. S., *J. Chem. Soc., A* 28 (1970).
139. Shibata, S., Bartell, L. S., and Gavin, R. M., Jr., *J. Chem. Phys.* **41**, 717 (1964).
140. Shirafuji, T., Yamamoto, Y., and Nozaki, H., *Tetrahedron Lett.* 4713 (1971).
141. Sidgwick, N. V., "The Chemical Elements and Their Compounds," p. 470. Oxford Univ. Press, London and New York, 1950.
142. Sleezer, P. D., Ph.D. Thesis, Univ. of California, Los Angeles, 1963.
143. South, A., Jr., Ph.D. Dissertation, Ohio State Univ., Columbus, Ohio, 1967.
144. South, A., Jr., and Ouellette, R. J., *J. Amer. Chem. Soc.* **90**, 7064 (1968).
- 144a. Stranks, D. R., and Yandell, J. K., *J. Phys. Chem.* **73**, 840 (1969).
145. Streitwieser, A., Jr., "Solvolytic Displacement Reactions," pp. 134-136. McGraw-Hill, New York, 1962.
146. Strohmeier, W., Humpfer, K., Miltenberger, K., and Seifert, F., *Z. Elektrochem.* **63**, 537 (1959).
147. Taylor, E. C., Altland, H. W., Danforth, R. H., McGillivray, G., and McKillop, A., *J. Amer. Chem. Soc.* **92**, 3520 (1970).
148. Taylor, E. C., Altland, H. W., McGillivray, G., and McKillop, A., *Tetrahedron Lett.* 5285 (1970).
149. Taylor, E. C., Altland, H. W., and McKillop, A., unpublished observations.
150. Taylor, E. C., Danforth, R. H., and McKillop, A., *J. Org. Chem.* in press.
151. Taylor, E. C., Hawks, G. H., III, and McKillop, A., *J. Amer. Chem. Soc.* **90**, 2421 (1968).
152. Taylor, E. C., Kienzle, F., and McKillop, A., *J. Amer. Chem. Soc.* **92**, 6088 (1970).
153. Taylor, E. C., Kienzle, F., Robey, R. L., McKillop, A., and Hunt, J. D., *J. Amer. Chem. Soc.* **93**, 4845 (1971).

154. Taylor, E. C., and McKillop, A., *Aldrichimica Acta* **3**, 4 (1970).
155. Taylor, E. C., and McKillop, A., *Accounts Chem. Res.* **3**, 338 (1970).
156. Taylor, E. C., Ochiai, M., and McKillop, A., unpublished observations.
157. Taylor, E. C., Robey, R. L., and McKillop, A., *Angew. Chem. Int. Ed. Engl.* **11**, 48 (1972).
158. Taylor, E. C., Robey, R. L., and McKillop, A., *J. Org. Chem.* **37**, 2797 (1972).
159. Traylor, T. G., *J. Amer. Chem. Soc.* **86**, 244 (1964).
160. Tyler, J. K., Cox, A. P., and Sheridan, J., *Nature (London)* **183**, 1182 (1959).
161. Uemura, S., Kitoh, R., Fujita, K., and Ichikawa, K., *Bull. Chem. Soc. Jap.* **40**, 1499 (1967).
162. Uemura, S., Kitoh, R., and Ichikawa, K., *Nippon Kagaku Zasshi* **87**, 986 (1966).
163. Uemura, S., Nakano, T., and Ichikawa, K., *J. Chem. Soc. Jap.* **88**, 1111 (1967).
164. U.S. Patent 2881007 (1958); *Chem. Abstr.* **52**, 16366 (1958).
165. U.S. Patent 3452047 (1969).
166. Weast, R. C., Ed., "Handbook of Chemistry and Physics," 49th ed., p. F-164. Chem. Rubber Co., Cleveland, Ohio, 1968.
167. Wiberg, K. B., and Koch, W., *Tetrahedron Lett.* 1799 (1966).
168. Wiley, R. H., and Wiley, P., *Chem. Heterocycl. Compounds* **20**, 13 (1964).
169. Wilkinson, G., and Cotton, F. A., *Prog. Inorg. Chem.* **1**, 10 (1959).
170. Winstein, S., and Roberts, R. M., *J. Amer. Chem. Soc.* **75**, 2297 (1953).
171. Wolf, W., and Kharasch, N., *J. Org. Chem.* **30**, 2493 (1965).
172. Yasuda, Y., and Okawara, R., *Organometal. Chem. Rev.* **2**, 225 (1967).
173. Zelesko, M. J., Ph.D. Thesis, Princeton Univ., Princeton, New Jersey, 1970.

The Radiochemistry of Organometallic Compounds

D. R. WILES

*Chemistry Department
Carleton University
Ottawa, Canada*

I. Introduction	207
II. Chemical Effects of Nuclear Transformations	208
A. Physical Aspects	208
B. Chemical Aspects	214
C. Some Chemical Problems	217
III. Survey of Experimental Results	221
A. σ -Bonded Compounds	221
B. π -Bonded Compounds	222
C. The Effects of β -Decay	234
IV. Discussion	237
A. Reaction Mechanisms	237
B. Applications to Other Fields	247
C. Future Trends	248
Note Added in Proof	249
General Bibliography	249
References	249

I

INTRODUCTION

When, in 1934, Szilard and Chalmers bombarded ethyl iodide with neutrons (86) they were searching for a sensitive method for detecting neutrons. The neutron capture gave rise to a radioactive isotope of iodine (^{128}I), largely as inorganic iodine, without there having been detectable bulk decomposition of the ethyl iodide. It seemed that the nuclear reaction had broken the carbon-iodine bond and selectively released the radioactive isotope. This so-called "Szilard-Chalmers" reaction was subsequently observed in many other nuclear reactions, and gave rise to numerous studies on enrichment of radioisotopes: permanganates, chromates, iodates, alkyl halides, metal phthalocyanines, many coordination compounds of cobalt, and other compounds have been extensively investigated during the period from 1935 to the present. Organometallic compounds were less frequently studied,

although the chemical effects of the β -decay of $^{210}\text{Pb}(\text{CH}_3)_4$ were observed (59) as early as 1934. The first serious investigation of radiochemical reactions in a metal-carbon-bonded compound was Maddock and Sutin's study of triphenylarsine (56) published in 1955. Since that time a wide variety of organometallic compounds have been studied: alkyl and aryl metals, simple and polymeric metal carbonyls, cyclopentadienyl metals, π -ring metal carbonyls, and others. The most interesting facet of these studies is perhaps the variety of radioactive metalorganic compounds produced other than the target compound, some of them previously unknown.

Several reviews¹ have been published of various aspects of "recoil" chemistry, "hot atom" chemistry, and "the chemical effects of nuclear transformations." In large measure, these have ignored the work on organometallic compounds, perhaps because these compounds cannot readily be classified along with the other types of compounds which make up the overwhelming bulk of this work: either the ionic compounds, the organic halides, or the ^{14}C and ^{11}C compounds. The present review is written primarily to bring to the attention of organometal chemists an area of their field which has hitherto been studied mostly by radiochemists, both in the hope that some of the methods developed by the radiochemists may be of wider use and with the recognition that the organometal chemists may more easily see solutions to problems for which the radiochemist's experience is insufficient. This review will thus give a brief description of the physical aspects of the nuclear reaction and subsequent atomic processes which occur in times too short to constitute conventional chemistry. Although the experiments are conceptually simple, they are not widely known and deserve clarification, if not detailed analysis. A short summary of interesting work of historical or practical significance will precede the main section, which will describe studies leading either to understanding of the phenomena occurring or at least to important questions.

II

CHEMICAL EFFECTS OF NUCLEAR TRANSFORMATIONS

A. Physical Aspects

Since most of the work to be described has been carried out with neutron irradiations, and since the physical phenomena accompanying neutron

¹ See General Bibliography.

capture typify the whole range of such physical effects, the process of neutron capture will be used to describe the physical aspects of our topic. Where differences arise from other nuclear processes, or where other reactions emphasize one aspect or another, this will be especially described in the appropriate section.

1. Neutron Capture and Decay Schemes

When a nucleus is placed in a flux of neutrons, it may capture another neutron. It thus is often unstable toward further decay by β^- -emission. The induced radioactivity is critical to the study of chemical consequences of neutron capture, since so few of these new nuclei are produced that generally they cannot be observed by any other means. This radioactivity is not, however, a part of the phenomenon which we wish to observe and, moreover, is occasionally a distraction.

The energy balance in neutron capture is easily accounted for by use of the law of conservation of mass-energy. Where a nucleus ^AN captures a neutron to become ^{A+1}N , we have the reaction energy, Q , given by

$$[M(^A\text{N}) + M(\text{n})] - M(^{A+1}\text{N}) = Q \quad (1)$$

For neutron capture in ^{55}Mn , for example, we have

$$[M(^{55}\text{Mn}) + M(\text{n})] - M(^{56}\text{Mn}) = 7.27 \text{ MeV} = 1.67 \times 10^8 \text{ kcal mole}^{-1}$$

Q values for neutron capture reactions are typically between 6 and 8 MeV. That the Q of the reaction has such a large positive value indicates that the ^{56}Mn is initially produced with its nucleus in a highly excited state, and that this energy must be dissipated, largely through radiative transitions. It is usually convenient to speak as though the energy were given off in a single γ -ray of 7.27 MeV, and one uses the notation (n, γ) to signify radiative neutron capture. While this is in part true, the real situation is complicated by the fact that a large number of nuclear energy levels lie between the initial excited state and the ground state. These intermediate states usually have lifetimes between 10^{-16} and 10^{-14} second, although if the spin change is large and the energy small, the lifetime can be much longer. Thus, a wide variety of deexcitation routes are possible, giving rise to capture γ -decay schemes (3) such as the one portrayed in Fig. 1. It is important to note that despite the large amount of work done on these deexcitation schemes, the complete decay paths are known for only a fraction of the decays. Thus in the case given, a fairly clear picture can be given for the dissipation of some

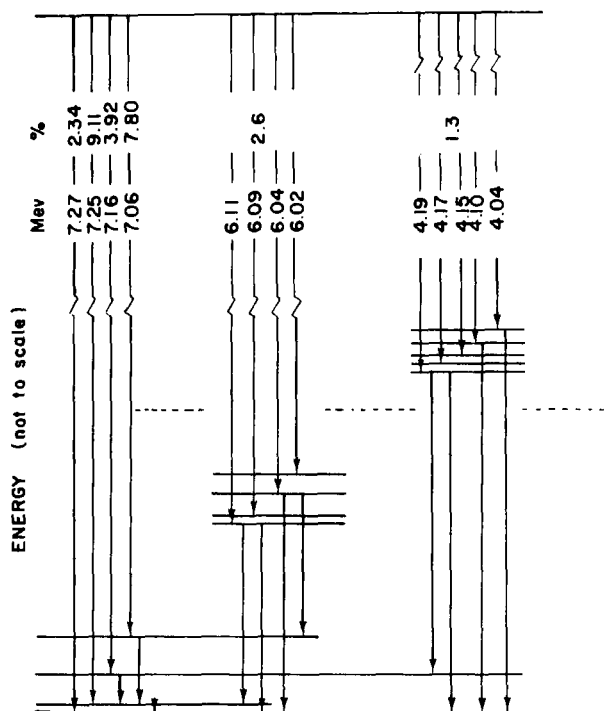


FIG. 1. Some representative γ -cascades from the observed neutron capture γ -spectrum of ^{56}Mn . From Bartholomew *et al.* (3).

60–70% of the energy, the rest being either as yet unobserved or not yet fitted into the decay scheme.

A further complicating factor is that many low-energy γ -transitions are converted, that is, their energy is released through the expulsion of one or more atomic electrons. This gives rise to the Auger cascade, which will be described below.

2. Recoil from γ -Emission

When a single γ -ray of known energy is emitted, the recoil energy given to the atom is calculated from the conservation of energy and momentum. The result is

$$E_R = \frac{p_\gamma^2}{2M} = \frac{E_\gamma^2}{2Mc^2} = 536 \frac{E_\gamma^2}{M} \quad (2)$$

where E_R is in electron volts if E_γ is expressed in million electron volts, and M in atomic mass units. Again using ^{55}Mn as our example

$$E_R(^{56}\text{Mn}) = 536 (7.27)^2 / 56 = 506 \text{ eV}$$

This recoil energy is so large compared to chemical energies that there seems to be no question about the atom's breaking loose from its bonds and travelling a considerable distance before coming to rest. The effect observed by Szilard and Chalmers is thus readily explained.

When a less simple nuclear deexcitation route is followed, the situation gets very complex. While in principle one must be able to add the momenta of all the γ -rays and calculate the resultant recoil momentum, in practice this cannot be done for enough events to make the calculation worthwhile. The two greatest contributing problems are that the angular correlation of the γ -rays is seldom known, and that the lifetimes of individual states may often be long enough that momentum may be lost to the surrounding medium even during the course of deexcitation.

Attempts have been made to calculate the recoil energy spectrum using an assumed statistical distribution of γ -energies and direction. Notably, Hsiung *et al.* (39) have done this calculation for ^{36}Cl produced by $\text{CCl}_4(n, \gamma)$. While the results of the calculation were in reasonable agreement with experimental data, the complexity of the necessary assumptions makes the agreement seem perhaps fortuitous.

Experimental determination of the recoil energy spectrum from neutron capture has not been reported.

3. Internal Conversion and Auger Ionization

Internal conversion of γ -transitions—the emission of a K or L electron instead of a γ -ray—occurs as a competitive deexcitation mode, especially when the transition energy is low and the angular momentum change is high, so that γ -emission is forbidden. It is also more probable for atoms of higher atomic numbers, in which the atomic and nuclear wave functions have a greater overlap. The result is that although this process does not compete favourably with emission of higher energy γ -rays, it is a probable mode of decay in the multiple low-energy cascades. It may, moreover, follow a higher energy γ -ray which leads to a low-lying excited state. Several of these deexcitation routes are easily discernible in Fig. 1.

It is evident that, since primarily only low-energy transitions are converted, the ultimate recoil energy will not be much affected whether a given transition is converted or not. The effect is felt in another way, however,

in that the low-lying electron vacancy gives rise to a cascade of X-ray or of Auger transitions.

The Auger effect is analogous to the internal conversion in that an atomic electron is emitted instead of the expected X-ray. Very little is well known about Auger yields in these transitions out beyond the K shell, and a more detailed discussion is outside the scope of this review.

It is very important that, at least in the gas phase, the ultimate result of an Auger cascade is rather extensive ionization of the atom or molecule concerned. A number of studies by Wexler and his colleagues and by Carlson and White have shown that single atoms may be left with a positive charge of up to 15 or more (89), while molecules may be atomized. The best example of this latter is the work (18) on $\text{Pb}(\text{CH}_3)_4$ in which an L vacancy was induced into the lead atom by X-ray irradiation. The resultant charged fragments were almost exclusively singly-charged atoms, and accounted for a total of 17 electrons emitted. These data are given in part in Table I. It is also significant that the lead atom was left with virtually zero kinetic energy, showing that the Coulomb explosion was centrosymmetric. A study of Auger effects in atomic manganese vapour (1) shows ions of $>+4$ to be less than 1% abundant, following single ionization in the L shell.

In the condensed state, unfortunately, practically nothing is known about the consequences of the Auger effect, although there is reason to believe that charge neutralization by electron transfer between neighboring

TABLE I
RELATIVE ABUNDANCES AND ENERGIES OF
IONS PRODUCED BY THE COULOMB
EXPLOSION OF $\text{Pb}(\text{CH}_3)_4^a$

Ion	Relative abundance	Energy (eV)
Pb^+	0.49	<0.05
Pb^{2+}	0.20	—
Pb^{3+}	0.10	—
$\sum \text{Pb}^{n+}$	1.00	—
C^+	1.9	13
C^{2+}	1.6	—
C^{3+}	0.22	—
H^+	10.4	29

^a Data from Carlson and White (18).

molecules is very fast. However, despite much speculation and some indirect evidence, it is still unknown whether or not the molecules are destroyed by Coulomb effects before the charge can be neutralized. There is need for a good deal of fundamental work on this question.

4. Anticipated Chemical Effects

From these various processes, one can separate at least three simple prototype pathways whereby the compound nucleus may get rid of its several million electron volts which constitute the neutron binding energy. These should encompass essentially all other possibilities, as far as chemical

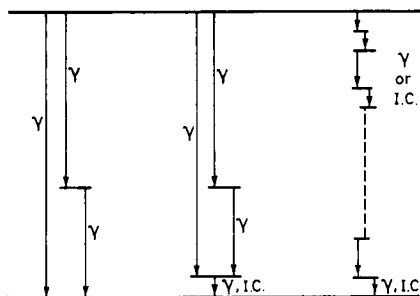


FIG. 2. Schematic representation of the types of γ -cascade, showing the origins of (i) pure recoil, (ii) recoil followed by Auger ionization, and (iii) Auger ionization with little or no recoil.

consequences are concerned. These deexcitation pathways, shown schematically in Fig. 2, are as follows:

- (i) Emission of one γ -ray with the total energy, or of a small number of high-energy γ -rays, such that considerable recoil energy results.
- (ii) Emission of one or more higher energy γ -rays followed by a converted low-energy transition.
- (iii) Emission of a larger number of γ -rays, of lower energy, of which one or more may lead to internal conversion and to the emission of Auger electrons, with little or no recoil.

These lead, respectively, to energetic recoil, to recoil followed by ionization, and to ionization *in situ*. The transitions for $^{56}\text{Mn}^*$ given in Fig. 1 are grouped according to these three alternatives. The logical fourth possibility—ionization followed by recoil—is in effect the same as the first

alternative inasmuch as the charge is soon neutralized in the course of the trajectory.

The fundamental question arising from this is whether the several radioactive products from a given sample arise from different reaction possibilities following the three deexcitation paths, respectively, or whether they arise rather through a statistical division of reactions following formation of essentially the same reactive intermediate from all three paths. There is as yet no clear answer to this question, although ion implantation experiments now underway promise to give a good indication.

B. Chemical Aspects

1. Methods and Definitions

The experiments are conceptually very straightforward although often more complicated in practice. A chosen target material is irradiated with neutrons (or other projectiles). Following the irradiation the target may, if desired, be thermally or otherwise treated (annealed) to effect solid-state reactions, after which the sample is dissolved and chemically processed in order to separate the various expected products and to measure their yields.

It is important to note that since the amounts of radioactive material produced are so extremely small (some 10^{-10} % of the total is typical) it is usually necessary to add macro quantities—10–100 mg—of each compound expected to be present, in order to effect a good separation and to measure the chemical yield of the carrier. The *yield* measured is the radioactivity in each separated chemical species as a fraction of the total radioactivity in the sample, corrected to 100% chemical yield of each respective carrier. The term “retention” is commonly used to refer to the yield of the parent compound. This term has the disadvantage, however, of implying that the radioactive atom *remained* in the same molecule. Since it often appears that the molecule is only later reconstituted, the terms “yield” and “parent yield” are to be preferred.

The total radioactivity, A_0 , of a specified nuclide in a target containing N atoms of the appropriate isotope, irradiated in a flux, f , of neutrons for t seconds and allowed to decay for T seconds after the end of the irradiation, is given by

$$A_0 = N\sigma f(1 - e^{-\lambda t})e^{-\lambda T} \quad (3)$$

where σ is the neutron capture cross section and λ the decay constant.

Of these radioactive atoms, a fraction F_i are produced in a specified form; the value of F_i may depend on the irradiation temperature, T , the γ -flux, and consequently on the irradiation time, t . This fraction may be altered by subsequent thermal treatment and by a variety of spurious reactions, to an extent expressible as $F'_i(t', T', \gamma' \dots)$. Thus, the activity of a given species, i , can be expressed as

$$A_i = N\sigma f(1 - e^{-\lambda t}) e^{-\lambda t'} F_i(t, T, \gamma) F'_i(t', T', \gamma' \dots) \quad (4)$$

The *yield* can be expressed as

$$Y_i \equiv A_i/A_0 = F_i(t, T, \gamma) F'_i(t', T', \gamma' \dots) \quad (5)$$

The two factors F_i and F'_i are very complex and not known. It is virtually certain, however, that each contains several terms. For example, where long-lived radiation-produced species influence the yield, F_i must contain terms such as $\lambda^{-1}\{1 - (\lambda t + 1)e^{-\lambda t}\}(1 - e^{-\lambda t})^{-1}$ which expresses the average age of the atoms produced. The subsequent thermal effects are often describable in terms of first-order reactions so that F'_i must contain one or more terms of the form $(1 - e^{-\lambda' t'})$. Up to the present, there has not been enough information available on any system to make careful statement of Eq. (5) worthwhile.

The details of the chemical methods need not concern us here, since they involve conceptually straightforward separations of compounds from one another. Some few special points are of interest, however, and concern largely potentially serious errors (which may all be found in the literature):

(1) Carrier-free species are apt to accompany other macrocomponents through the separation procedures, especially sublimation.

(2) Sublimation without prior dissolution is likely to cause thermal annealing effects. Even dissolution of the samples at room temperature may cause thermal reactions to occur, although these, at least, are usually reproducible.

(3) Exchange and other spurious reactions are often difficult to avoid. Carriers, scavengers, and the like should be added to the solvent before dissolution of the sample. Even then exchange is possible.

(4) Failure to measure chemical yields and to identify products are sometimes difficult to rectify, especially in the case of unexpected carrier-free compounds. Unfortunately, the amounts involved are so small that even the

most sensitive instrumental methods—ESR, for example—are not useful in making the identifications.

2. General Nature of the Results

The earliest studies in this field were conducted largely to benefit from the Szilard-Chalmers effect—namely, the separation of radioactive atoms from the bulk material—in order either to make nuclear chemical study of radioactive nuclides or to effect an enrichment of radioisotopes. In Table II are listed some selected works of this type.

TABLE II
EARLY STUDIES OF ISOTOPE ENRICHMENT BY THE SZILARD-CHALMERS EFFECT

Target compound	Isotope	Enrichment factor	References
$(\text{CH}_3)_3\text{AsCOOH}$	^{76}As	—	82
Uranyl benzoylacetate	^{239}Np	—	83
$\text{UO}_3 + \text{Cr}(\text{CO})_6$	$^{103}, ^{104}, ^{105}\text{Mo}$	—	52
$(\text{C}_6\text{H}_5)_3\text{Sb}$	$^{122}, ^{124}\text{Sb}$	500	94
Metal phthalocyanines of Zn, Ga, In, V, Mo, Pd, Os, Ir, Pt		≥ 1000	35
$\text{Cr}(\text{CO})_6$	^{51}Cr	10^4	87
R_2Hg	^{197}Hg , etc.	$\sim 10^3$	32
$\text{Sn}(\text{C}_6\text{H}_5)_4$	^{124}Sn	2×10^3	79
$(\text{C}_2\text{H}_5)_4\text{Ge}$	^{75}Ge	—	66

Study of the “recoil” chemistry of organometallic compounds for its own sake, began really in 1955 with the publication of a study (56) by Maddock and Sutin on neutron activation of triphenylarsene. Since this time, most of the published work has been focussed on those radioactive atoms which did *not* permanently escape their ligands. Thus, in one way or another, they end up in molecular form. It is with these that this review is largely concerned.

In general, an appreciable retention or parent yield is found, which may vary from 5–6% up to 60–70%. Occasional lower or higher values can usually be attributed to spurious reactions. The yields of other products is usually somewhat lower. In some target compounds no other stable product is expectable, as in FeCp_2 , $\text{Cr}(\text{CO})_6$, $\text{Ni}(\text{CO})_4$, $\text{Cr}(\text{C}_6\text{H}_6)_2$. In other cases,

where two types of ligand are present already in the target molecule, competitive reactions may give rise to two or more side products: $(\text{PhH})_2\text{Cr}$ and $\text{Cr}(\text{CO})_6$ from $\text{PhHCr}(\text{CO})_3$, FeCp_2 , and $\text{Fe}(\text{CO})_5$ from $[\text{CpFe}(\text{CO})_2]_2$, and so on. Still a third possibility is that of the formation of new ligands from fragments of dissociated ones. This is likely only to produce σ -bonded ligands, whether one starts with σ - or with π -bonded ligands. Thus HAsPh_2 can be formed from AsPh_3 , $\text{H}_2\text{Ge}(\text{C}_2\text{H}_5)_2$ from $\text{Ge}(\text{C}_2\text{H}_5)_4$, $\text{CH}_3\text{Mn}(\text{CO})_5$ from $\text{CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{CO})_3$, and others.

In a number of cases products have been obtained which have as yet not been identified. These are often very difficult to study, being present in such extremely small amounts, and their presence is sometimes only inferred from a decreasing yield of the parent upon further purification. Usually the yields of the unidentified products are small enough that they can be ignored in attempting to understand the product spectrum. In some cases compounds have been synthesized which were not previously known, such as $\text{CpTc}(\text{CO})_3$, $\text{Tc}(\text{C}_6\text{H}_6)_2^+$, PmCp_3 , and others.

C. Some Chemical Problems

Throughout the studies discussed in this review there persist a number of questions of so fundamental a nature as to preclude much further progress in the field before additional insight is available. These involve areas in which decisive experiments have not yet been done, and in which such experiments appear to be either very difficult or totally impossible. These questions arise: What is the nature of the starting species? What effects result from reactions extraneous to the radiochemical phenomenon—adsorption, exchange, etc.? At what stage following the nuclear event do the observed chemical reactions occur?

1. Bond Rupture and the Starting Species

The starting species has often been assumed to be the single radioactive atom recoiling away from its point of origin and from its original ligands. While this may often be true, there are various difficulties about this being the only starting point. Experimentally, only a very few studies have been made of the extent of failure of bond rupture, and only one on organometallic compounds. Zahn (97) found that solid $\text{CpMn}(\text{CO})_3$ has a parent yield of 12.7% but that when the target compound is irradiated in dilute

benzene solution the parent yield decreases to a minimum value of 0.016%. This she took to represent the extent of failure of bond rupture. This experiment, however, does not distinguish between total bond rupture and partial bond rupture, and gives the extent of total failure of bond rupture. Species such as $\text{Mn}(\text{CO})$, $\text{Mn}(\text{CO})_2$, CpMn , and others could still be the most primitive species involved.

On the basis of assumed total molecular fragmentation, a very simple axiom was stated by Narayan and Wiles (61): "The simpler is the target molecule, the greater should be the probability of reforming the parent compound." That this axiom is spectacularly violated in virtually every case in which it has been put to test may indicate that the complex molecules have a particular resistance to bond rupture. For example, cyclopentadienylmanganese tricarbonyl, $\text{C}_5\text{H}_4\text{Mn}(\text{CO})_3$, shows a parent yield of 6% (44). The "dimeric" fulvalene dimanganese hexacarbonyl, $[\text{C}_5\text{H}_4\text{Mn}(\text{CO})_3]_2$, has a parent yield of some 9.1% (47) despite the prediction of the axiom. It may well be, then, that the recoil energy has a good chance of being dissipated throughout the molecule before the recoil atom can leave its immediate neighborhood. This chance of energy dissipation ought to be related to the number of degrees of freedom of the molecule and thus to contradict the above axiom. Similar arguments may apply to $\text{Ru}_3(\text{CO})_{12}$, $\text{Fe}_3(\text{CO})_{12}$, and $[\text{CpFe}(\text{CO})_2]_2$, all of which have much higher parent yields than the axiom would allow.

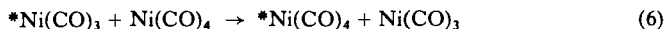
Another approach to the same problem involves secondary reactions of simpler building blocks such as, in the cases mentioned, $-\text{C}_5\text{H}_4\text{Mn}(\text{CO})_3$, $\text{Ru}(\text{CO})_4$, $\text{Fe}(\text{CO})_4$, and $-\text{FeCp}(\text{CO})_2$. In any event, one is left with the probability that at least some part of the molecule remained intact after the nuclear event, in order to account for the high yields.

It is convenient, and usually satisfactory, to assume that at least the ligands remain intact. Even this is not always necessarily correct, in view of Harbottle's demonstration that ^{11}C is able to reform CO and then reform $\text{Cr}(\text{CO})_6$ quite efficiently (30).

In some cases the ligands have been found to decompose. Notably the study of germanium tetraethyl by Nowak and Akerman (67) showed that ethyl groups could be reconstituted as methyl, vinyl, and others. Methylmanganese pentacarbonyl was found (81) from neutron-irradiated methylcyclopentadienylmanganese tricarbonyl. It has not yet been shown whether these are formed through radiochemical effects or through subsequent radical exchanges. Radiation effects seem also to be involved.

2. Exchange Reactions

Exchange reactions and other radiochemically trivial processes are often difficult to eliminate and must be considered as possibly contributing to virtually all observed yields. In the case of Ni(CO)_4 , for example, the exchange of CO in the liquid is so fast that the full 98.7% observed parent yield (92) can be explained on the basis of the exchange reaction

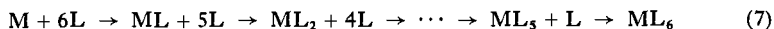


In other cases normal exchange can be virtually eliminated by comparison of the experimental times involved with the half-time for exchange.

The validity of these macroscale arguments is questionable, however, when microquantities are involved, or when abnormally reactive fragments may be present.

3. The Time of the Reactions

The time at which the reactions occur is, of course, of vital importance in helping to arrive at reasonable views of possible mechanisms, and represents one of the most tantalizing questions in the field. While at one time it was thought possible that the reactions could be simple, high-energy, billiard-ball collisions (54, 58), the likelihood of that occurring is small (95) and in any event could not account for the formation of compounds other than the parent. It is probable that the reformation of most molecules occurs in a stepwise fashion:



although, as was explained above, there is no certainty as to where this chain of reactions begins.

It is also possible that the last step may occur during dissolution just before separation, or in the solid as the sample is warmed up to room temperature. The first of these can, in fortunate cases, be intercepted, so as to form a selected compound from a radical or other incomplete molecule in the solid (46). There are several examples of the second—room-temperature annealing—and it is useful when possible to dissolve the target at low temperature.

Two means are available for learning about the time at which reactions occur. One can vary the conditions of the irradiation—the time, temperature, and γ -flux—in order to alter the value of $F(t, T, \gamma)$ of Eq. (4). The other, rather more versatile, approach is to perform various treatment on the

sample after the irradiation—to vary the value of $F'(t', T', \gamma' \dots)$. If the yield of a given species is insensitive to any variation of experimental conditions, it is probably safe to assume that the molecules were already formed by the time the atom became sensitive to its surroundings: that is, while the atom's immediate surroundings were still highly excited. On the other hand, a product whose yield is sensitive to post-irradiation thermal treatment must be formed, at least in part, by a temperature-sensitive process which occurred during the annealing. If the yield is affected by the irradiation temperature, then the reaction must be a fast thermal reaction, likely of low activation energy.

Activation energies have been studied in the case of solid ionic compounds, where the target compounds and their side products are somewhat more stable and easier to handle. No measurements of activation energies have as yet been made on organometallic compounds, and unfortunately, very few annealing studies have been done.

If the yield of a given radioactive product is sensitive to the presence or absence of scavengers during any part of the operation (and if the bulk carrier compound is also present during the scavenging), it is customary to conclude that the scavenging had intercepted the reformation reaction before the final stage. Unfortunately, it is not possible with most organometallic compounds to use scavengers at a stage earlier than the dissolution of the crystals. Nath *et al.* (62) have found a marked effect of the atmosphere (O_2 , N_2 , vacuum, etc.) during the annealing of the cobalt complexes tris(acetylacetonate)cobalt(III) and bis(salicylaldehyde)triethylenetetramine cobalt(III) chloride. They found that in both cases the extent of thermal annealing, but not the rate, was suppressed by an electron-donating atmosphere. This led them to the conclusion that the reaction involves shallow electron traps, both at the surface and within the crystal. Zahn *et al.* (99) have used a similar approach by showing a strong dependence of the annealing of $Cr(CO)_6$ on the presence of CO under pressure. In this case neutral CO molecules were inferred to be reacting.

One further approach, which has not properly been explored, is based upon the axiom of Harbottle's (29) that if an isotopic difference is found, there must have been little reaction subsequent to the initial hot stage. That is, these subsequent reactions are expected to be normal chemical reactions with essentially no isotopic preference, such that any such reaction would tend to wash out possible isotope effects. This problem is worth pursuing further, since some isotopic effects have been observed where subsequent exchange is to be expected.

III

SURVEY OF EXPERIMENTAL RESULTS

We shall divide the experimental work according to whether the bonding is primarily σ or π . The difference is subtle and may turn out to have been more apparent than real. Compounds in which bonding is mixed, as in $\text{RMn}(\text{CO})_5$, will be considered with the π -bonded compounds.

A. σ -Bonded Compounds

Both alkyl and aryl metals have been studied, but not a very wide range of compounds. Several studies of triphenylarsene and triphenylstibine have been done. Methyl and ethyl compounds of arsenic, germanium, mercury, bismuth, and lead essentially complete the list. In virtually all cases the results have been clouded by difficulties in effecting chemical separation without altering the product distribution. The results do, nonetheless, lead to valid and important conclusions.

Maddock and Sutin (56) observed the formation of numerous oxygenated products in neutron-irradiated AsPh_3 which, they argued, must have come from reaction of AsPh_x radicals with oxygen or water during the separation. The annealing effect of heating at 45° led to increased yields of AsPh_3 , while AsPh_2 products first increased and then decreased. This was interpreted as showing the involvement of phenyl radicals in a series of consecutive reactions:



A series of studies by the Polish group of Siekierska, Sokolowska, and Halpern supported and extended this work. By irradiating benzene solutions of AsCl_3 and finding good yields of AsPh and AsPh_2 compounds (but not AsPh_3) they were able to prove (77) that neither billiard-ball reaction nor preservation of original bonds was necessary for formation of phenyl arsenic compounds. A similar investigation of benzene solutions of AsPh_3 showed a marked scavenging effect of oxygen and of AsCl_3 which led them (75, 76) to an independent statement of the above conclusion of stepwise radical reactions. They were able, moreover, to separate the reactions leading to the various products into (1) failure of bond rupture, (2) hot reactions,

and (3) thermal reactions, on the basis of the scavenger effects (75). Further support for the involvement of radical reactions in benzene-AsCl₃ solutions was an increased yield of AsPh compounds following application of an external γ -field, suggesting a diffusion-controlled reaction with radiation-produced phenyl radicals (33).

A very extensive and detailed study of the phenyl arsenic system was published by Grossmann (24-27), who also made a thorough study of separation methods and was able to effect a reliable separation of the products according to the number of phenyl groups attached to the arsenic. His results supported the earlier work and added the interesting observation that arsenic-containing radicals can be scavenged (presumably by hot reactions) by oxygen atoms from within the target compound itself.

Nowak and Akerman (66, 67) have studied neutron-irradiated Ge(C₂H₅)₄ and observed a large number of products, involving hydrogen, methyl, ethyl, butyl, and vinyl groups bonded to the germanium. The yields of several of the products were fairly sensitive to changes in the γ -dose (50 Mrad vs. 2.5 Mrad), which led Nowak and Akerman to the conclusion that some of the main reactions involved radiation-produced radicals and scavengers.

Work on mercury alkyls has been done by Heitz and Adloff (31-33), who studied Hg(CH₃)₂, Hg(C₂H₅)₂ and HgPh₂. They found no isotope effect between ^{197m}Hg, ¹⁹⁷Hg, and ²⁰³Hg, and no correlation with the respective conversion coefficients. They also noted that the retentions could not be satisfactorily explained by exchange of the respective ligands, and thus concluded that the molecules are reformed by an epithermal not by a thermal process. Parent yields were typically 74, 15, and 8% for the diphenyl-, dimethyl- and diethylmercury, respectively.

B. π -Bonded Compounds

The distinguishing feature of π -bonded compounds in this context is that a fragmented ligand can no longer give rise to the same type of compound if, indeed, to a stable compound at all. While it is possible that atoms of C and O may rapidly re-form a CO molecule which is then able to react further, the fragments of cyclopentadiene cannot be expected to arrange themselves so as to reform the original or any other π -bonding ligand. The molecule is thus destroyed unless it can be reformed by an exchange reaction, or replaced by another molecule in which one or more ligands is σ -bonded.

1. π -Ring Compounds

We shall single out $\text{Cr}(\text{C}_6\text{H}_6)_2$, $\text{Ru}(\text{C}_5\text{H}_5)_2$, and $\text{Fe}(\text{C}_5\text{H}_5)_2$ for discussion, although several other "sandwich" compounds have been studied: $\text{Ni}(\text{C}_5\text{H}_5)_2$ and $\text{Co}(\text{C}_5\text{H}_5)_2$ (72, 90), and $\text{Hf}(\text{C}_5\text{H}_5)_2\text{Cl}_2$ and $\text{Zr}(\text{C}_5\text{H}_5)_2\text{Cl}_2$ (36, 91).

The early work of Sutin and Dodson (85) on neutron-irradiated ferrocene exemplifies the results and problems of recoil chemistry. After dissolving their samples in hexane and extracting with aqueous solutions they isolated, after further purification, radioactive FeCp_2 and a species which emerged as ionic iron(III). Adsorbed on the walls of the glass vessels remained another species soluble in acetone which accounted for up to 50–60% of the radioactive iron. This species has not yet been identified. The FeCp_2 activity accounted for some 10–12% of the ^{59}Fe , which increased on standing several weeks at room temperature or 2–3 days at 110° C, as is shown in Table III.

TABLE III
PARENT YIELDS (RETENTIONS) OF ^{59}Fe IN FERROCENE^a

Irradiation	Initial yield		After storage (20° C)
	(%)		
50°–60° C, 270 Mrad	12	42 days	19%
20° C, 0.1 Mrad	12	42 days	14.4%
–78° C	10.8	22 days	24.6%
–196° C	9.6	6 days	14.3%

^a Data from Sutin and Dodson (85) and Hillman and Weiss (37).

The authors speculate that the observed effect of standing or heating involves a reaction of species such as $^{59}\text{FeCp}$ with an additional Cp formed during the irradiation by the recoil of the Fe atom or by fast neutron damage.

Also interesting is the solid-state interaction between the water-extractable fraction and the acetone-soluble fraction. Heating of the irradiated ferrocene at 110° C causes a sharp decrease in the water-extractable activity (from 55 to 15% in 2–3 hours). This 40% does not appear as ferrocene and is assumed to form some stable molecular species other than ferrocene.

Since this change in distribution of the radioactive iron occurs most strongly in samples which have suffered a heavy fast neutron bombardment, one surmises that there must be a reaction with the products of bulk radiation damage. The products have not been identified.

Recent work (51) on $^{56}\text{FeCp}_2$ irradiated in $^{58}\text{Fe}(\text{CO})_5$ solutions (to give $^{59}\text{FeCp}_2$) has shown that the ^{59}Fe atom can come from the $\text{Fe}(\text{CO})_5$ molecule. The mechanism is unknown and may well involve exchange or other reactions in solution in addition to hot atom reactions. The results do show, however, that it is not necessary to *preserve* the Fe-Cp bonding in order to reform FeCp_2 . In frozen solutions the yield of $^{59}\text{FeCp}_2$ is much lower than in liquid solutions.

Formation of $^{59}\text{FeCp}_2$ is also noted in neutron-irradiated $[\text{CpFe}(\text{CO})_2]_2$, as will be described later. An important difference here is that the radioferrocene seems to be formed in the dimeric carbonyl only by very fast solid-state reactions.

It is interesting to note that neutron irradiation of ferricinium picrate (40) produced only 2.2% of the ^{59}Fe as FeCp_2^+ , which yield was not increased on subsequent heating. The authors suggest that the difference between FeCp_2 and FeCp_2 picrate may be due to an increased stopping power of an ionic lattice, leading to the production of fewer reactive fragments. In view of the results given above from Grossmann (25), it is perhaps more likely that the oxygen atoms from decomposed citrate ions are scavenging the iron atoms to form an iron oxy compound before the reaction with cyclopentadienyl radicals can occur.

The radiochemistry of ruthenocene has been studied by Baumgärtner and Reichold (9) and by Harbottle and Zahn (29). It is found that neutron irradiation of crystalline RuCp_2 yields about 10% of the radioactive ruthenium as $^*\text{RuCp}_2$. More specifically, an isotopic difference in the radiochemical yield is found: ^{97}Ru , $9.6 \pm 0.1\%$; ^{103}Ru , $10.7 \pm 0.2\%$; and ^{105}Ru , $9.9 \pm 0.2\%$ (29). In liquid solution the isotopic effect is much more pronounced, although the yields are lower. This was suggested by Harbottle as a general principle: the greatest isotope effects are associated with the lowest yields. While this principle has not yet been substantiated, it seems reasonable since any thermal reactions which may increase the yields would not likely show any isotope effect.

Aside from the incorporation of rutheruthenium in the parent RuCp_2 , a number of other interesting things have been observed. Baumgärtner and Reichold (9) found, on bombarding a powdered mixture of FeCp_2 and

U_3O_8 , that a considerable portion (up to 60%) of the fission-produced ^{105}Ru is recoverable as $^{105}\text{RuCp}_2$. Zahn and Harbottle found, moreover (100), that on bombardment of uranium foil in contact with liquid monomeric cyclopentadiene (but not with dimeric) a large amount of $^{105}\text{RuCp}_2$ is produced. These crucial experiments show that neither the metal atom nor the Cp ligand need have formed Ru-Cp bonds previously, although at least the Cp must be in a rather reactive state for reaction to occur. Reichold (69) found, however, that even when $\text{K}_4^{105}\text{Ru}(\text{CN})_6$ and FeCp_2 are simply ground up together in a mortar, some $^{105}\text{RuCp}_2$ is formed.

Both types of experiment [fission + FeCp_2 and RuCp_2 (n, γ)] seem to yield additional volatile ruthenium compounds. These compounds have not yet been identified.

Dibenzenechromium was studied by Baumgärtner *et al.* (15). They found that the yield of $^{51}\text{Cr}(\text{Ph})_2$ was 11.8%. [One cannot fail to be struck by the similarity in yields of FeCp_2 , RuCp_2 , and $\text{Cr}(\text{PhH})_2$, although it may well be merely coincidence.] On heating the irradiated samples to 110°C , they found the yield to increase to 19.4%. It was found that dissolution of the radioactive crystals in benzene yielded no further $^{51}\text{Cr}(\text{PhH})_2$. This stands in contrast to the above-mentioned results of Zahn and Harbottle which, though not strictly comparable, show Cp to be quite reactive toward ruthenium atoms. Dibenzenechromium was also formed in low yield (14) from neutron irradiation of $\text{PhHCr}(\text{CO})_3$, as will be discussed in more detail later.

2. Metal Carbonyls

Carbonyl compounds of Cr, Mo, W, Ni, Mn, Re, Ru, and Fe have been studied. Of these the Group VI hexacarbonyls have received by far the greatest attention. Generally the yields are all fairly high and often dependent upon radiation and thermal conditions. The data for (n, γ)-activated samples, without radiation or thermal treatment, are summarized in Table IV. Thermal treatment of Cr and Mo hexacarbonyls has been done by Collins and by Harbottle and their co-workers. The recent isochronal annealing study by Groening and Harbottle (23) has shown a stepwise reformation of $\text{Mo}(\text{CO})_6$ as a function of temperature, shown in Fig. 3. This interesting result suggests the involvement of reactions with three or four distinct activation energies. The reactions giving rise to these steps have not been identified, but clearly must involve carbonyl transfer from different sites, both bound and unbound. The hypothesis here is that the reaction of

TABLE IV
SUMMARY OF YIELDS OF RADIOACTIVE PARENT
COMPOUND IN THE METAL CARBONYLS, WITHOUT
SUBSEQUENT ANNEALING

Compound	Yield	References
$\text{Cr}(\text{CO})_6$	40 ^a	99
$\text{Mo}(\text{CO})_6$	60 ^{a, b}	23, 34, 99
$\text{W}(\text{CO})_6$	50–60 ^a	61, 99
$\text{Fe}(\text{CO})_5$	41 ^c	61
$\text{Ni}(\text{CO})_4$	98.7	92
$\text{Mn}_2(\text{CO})_{10}$	12–14 ^{a, d}	44, 46
$\text{Re}_2(\text{CO})_{10}$	5–6 ^a	88
$\text{Ru}_3(\text{CO})_{12}$	41	61
$\text{Fe}_3(\text{CO})_{12}$	26 ^e	61

^a The yield is dependent on the radiation dose.

^b Isotope effect observed.

^c 26% of the ⁵⁹Fe was found as $\text{Fe}_3(\text{CO})_{12}$.

^d 4.5% of the ⁵⁶Mn appears as $\text{Mn}(\text{CO})_5$.

^e 17% of the ⁵⁹Fe is $\text{Fe}(\text{CO})_3$.

$\text{Mo}(\text{CO})_n$ is with “trapped” CO groups whose “trapping” energies differ, as well as the relative site populations. Although Zahn, Collins, and Collins did not observe these steps, their choice of temperature is such as not to contradict the stepped formation. The puzzling feature of this step formation is that the steps were different, both in position, in height, and in number, for the isotopes ⁹⁹Mo and ¹⁰¹Mo. On the basis of present understanding, one would expect the two isotopes to show steps of different heights but not at different temperatures nor different in number.

The role of excess carbon monoxide in the thermal treatment of $\text{M}(\text{CO})_6$ was clearly shown by Zahn *et al.* (99), who performed thermal annealing of $\text{Cr}(\text{CO})_6$ under CO pressure. The yield of ⁵¹Cr(CO)₆ was greatly increased by both heating and pressure, much less by heating alone, and very little by CO alone. Some illustrative data are given in Table V. The rather strong effect of concomitant γ -radiation dose was interpreted as resulting from radiolysis of the carbonyl to make more CO molecules available for reaction. The fact that this γ -effect showed up more strongly in annealed samples than in unannealed signifies that the γ -radiolysis was not spatially correlated with the (n, γ) event.

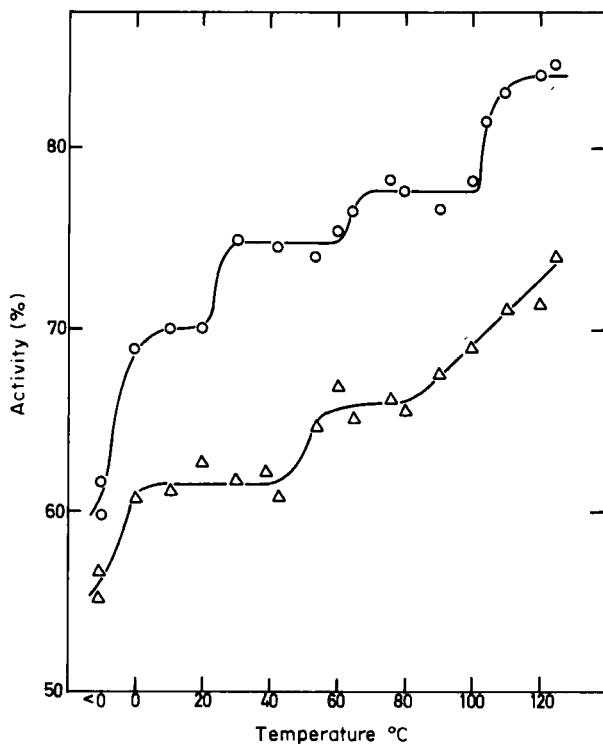


FIG. 3. Stepwise thermal annealing effect in Mo(CO)_6 . From Groening and Harbottle (23).

TABLE V

PARENT YIELDS IN Cr(CO)_6 ANNEALED UNDER CO PRESSURE^a

Annealing	CO pressure	$^{51}\text{Cr(CO)}_6$ (%)
None	None	43.7
120 min, 120° C	None	60.2
120 min, 22° C	100 atm	49.3
120 min, 80° C	100 atm	74.4
120 min, 120° C	100 atm	78.8
1 Mrad γ -rays, 22° C	None	44.5

^a Data from Zahn *et al.* (99).

The results of this study show (99) the involvement of fragments such as $\text{Cr}(\text{CO})_x$ ($3 \leq x \leq 6$) which react with CO molecules which come from any of several sources: fragmentation of the original molecules, bulk radiolysis of the compound, application of an external atmosphere, or perhaps from intermolecular exchange. It was concluded from the data that diffusion processes are involved and that the relative rates of reaction and of diffusion away are important in determining the height of the annealing plateaus.

The wealth and complexity of information coming from this study suggest that further detailed investigation of the radiochemical behavior of this compound would be very rewarding. One such study, apparently confirming the above-described work, has not yet been published in full (101).

An earlier study by Baumgärtner and Reichold (11) shows further that even single metal atoms can react with available CO molecules to produce carbonyls. By irradiating a mixture of powdered $\text{Cr}(\text{CO})_6$ and U_3O_8 , they were able to catch the fission product ^{99}Mo and isolate it as $\text{Mo}(\text{CO})_6$. This clearly indicates that molecule formation is not dependent on previously formed bonds. The yields of $^{99}\text{Mo}(\text{CO})_6$ (60%) were too high to represent only the primary fission product molybdenum atoms, and indicate that some short-lived precursors of ^{99}Mo (^{99}Zr , ^{99}Nb) may also have formed at least tentative metal-CO bonds, and produced $\text{Mo}(\text{CO})_6$ after β -decay.

Significant experiments have been done by Harbottle and Zahn (30) and by Henrich and Wolf (34), studying reactions of higher energy. Yields in $\text{Cr}(\text{CO})_6$ following (γ, n) , (p, pn) , and $(p, p2n)$ were all high (30)—70–84%—higher, in fact, than the yield from (n, γ) . Since the first three nuclear reactions produce nuclei at much higher energies than does the (n, γ) reaction, these higher yields were attributed to greater availability of reactive CO groups by virtue of local radiation damage. Yields of ^{11}C -labeled $\text{Cr}(\text{CO})_6$ were lower, but still quite substantial—30–40%.

Yields of $^*\text{Mo}(\text{CO})_6$ have given somewhat contradictory results regarding isotopic differences. Harbottle and Zahn find no significant difference between yields of $^{90}\text{Mo}(\text{CO})_6$ (75.0%) and $^{99}\text{Mo}(\text{CO})_6$ (73.7%) produced by high-energy recoil. Coupling these with their results for $\text{Cr}(\text{CO})_6$, they concluded that the reactions leading to formation of the product molecules are thermal reactions, retaining no memory of the nuclear reaction or subsequent deexcitation. Henrich and Wolf, on the other hand, find a marked isotopic difference between $^{90}\text{Mo}(\text{CO})_6$ and $^{93\text{m}}\text{Mo}(\text{CO})_6$, an effect which seems to be independent of recoil energy over a considerable range. They conclude that the products formed are sensitive to the occurrence of excited

states whose half-lives are greater than the time for slowing down of the projectile atom ($>10^{-8}$ second).

These data do show, in any case, that there is no need to retain any bonding to a CO group, since the species recoiling at high energy is certainly a single atom (or ion).

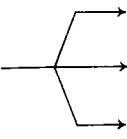
The several polymeric metal carbonyls studied have led to some surprisingly high yields [e.g., $\text{Fe}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_{12}$ in Table IV] but to no substantiated mechanisms. The 17% yield of $\text{Fe}_3(\text{CO})_{12}$ in neutron-irradiated $\text{Fe}(\text{CO})_5$ was interpreted as a reaction of $\text{Fe}(\text{CO})_4$ with the $\text{Fe}(\text{CO})_5$, but no further evidence is available. The study of $\text{Mn}_2(\text{CO})_{10}$ has been fruitful (44, 46). The insensitivity of the parent yield $^{56}\text{MnMn}(\text{CO})_{10}$ to heat indicates that the molecule is formed by a reaction quite early in the sequence, perhaps epithermal. The discovery (46) of a species which reacts rapidly with I_2 and exchanges with $\text{IMn}(\text{CO})_5$ led to the conclusion that the $\cdot\text{Mn}(\text{CO})_5$ radical is produced prominently (4.5%) by nuclear reactions in the solid decacarbonyl. The availability of this labeled $\cdot^{56}\text{Mn}(\text{CO})_5$ has made possible several interesting observations about the exchange properties of this radical in the solid (45) and in solution (42).

3. Mixed π -Ring Carbonyl Compounds

The interesting feature of mixed π -ring carbonyl compounds lies in the possibility of observing competitive reactions between the two ligands. As yet very few systems have been studied, largely because such systems seldom have a favorable combination of chemical properties (stability and easy separability of all expected compounds) and nuclear properties (capture cross section, half-life, and radiation energy).

The first such compound to be studied was benzenechromium tricarbonyl (14), which gave the results shown in Table VI. The striking thing about

TABLE VI
RADIOCHEMICAL YIELDS OBTAINED FROM $\pi\text{-C}_6\text{H}_6\text{Cr}(\text{CO})_3$ ^a

$\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ (n, γ)		$\text{Cr}(\text{CO})_6$	13.5%
		$\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$	10.0%
		$(\text{C}_6\text{H}_6)_2\text{Cr}$	0.2%

^a Baumgärtner and Zahn (14).

these data is, of course, that the hexacarbonyl is formed in such high yield compared to that of the dibenzenechromium.

A series of studies on CpMn(CO)_3 and related compounds showed similarly that $-\text{Mn(CO)}_5$ compounds are formed in substantial yield. The yield of MnCp_2 could not be assessed properly inasmuch as the carrier seems to exchange rapidly with some radioactive species not containing cyclopentadiene (80). The data for various manganese-containing compounds are summarized in Table VII. In addition to those compounds reported in the table, two other, as yet unidentified, radioactive compounds were found in neutron-irradiated CpMn(CO)_3 (20).

TABLE VII
RADIOCHEMICAL YIELDS IN SOME MANGANESE COMPOUNDS, FOLLOWING
NEUTRON ACTIVATION

Target	Compound	Yield (%)	References
CpMn(CO)_3	CpMn(CO)_3	7.0	44
		11.7 ^a	98
		12–20 ^a	20
	HMn(CO)_5	10–12	44
	$\text{Mn}_2(\text{CO})_{10}$	0.4	44
$\text{CH}_3\text{CpMn(CO)}_3$	$\text{CH}_3\text{CpMn(CO)}_3$	8	44
	$\text{CH}_3\text{Mn(CO)}_5$	2	44
	HMn(CO)_5	10	44
$\text{C}_{10}\text{H}_8\text{Mn}_2(\text{CO})_6^b$	$\text{C}_{10}\text{H}_8\text{Mn}_2(\text{CO})_6^b$	9.1	47
	CpMn(CO)_3	0.2	47
	HMn(CO)_5	4 ^c	47
	$\text{Mn}_2(\text{CO})_{10}$	0.25	47

^a These values may reflect either a radiation sensitivity or the presence of varying amounts of HMn(CO)_5 .

^b Fulvalene dimanganese hexacarbonyl: $(\text{OC})_3\text{MnCp-CpMn(CO)}_3$.

^c Obtained as IMn(CO)_5 by reaction with I_2 .

A number of significant features appear in this table, in addition to the evidence for $-\text{Mn(CO)}_5$ compounds. Since no $\text{CH}_3\text{Mn(CO)}_5$ was obtained from CpMn(CO)_3 , the methyl group must clearly come from the ring substituent unless another source of $-\text{CH}_3$ is present. Samples of $\text{CH}_3\text{CpMn(CO)}_3$ diluted with 2,2,4-trimethylpentane yielded up to ten

times more $\text{CH}_3\text{Mn}(\text{CO})_5$, depending on the concentration. It is apparent that radical reactions are occurring in this situation: Yang (96) found a typical scavenger action on the part of small amounts of acetone added to benzene solutions of $\text{CH}_3\text{CpMn}(\text{CO})_3$ prior to irradiation. Srinivasan found (44) that 2,2,4-trimethylpentane added to the same target compound first increased then at progressively higher concentrations decreased the yield of $\text{CH}_3\text{Mn}(\text{CO})_5$, as apparently the concentration of radiolytic $-\text{CH}_3$ increased and then other competitive reactions set in. Moreover, a small amount of $\text{Fe}(\text{CO})_5$ added to the solution quenched the formation of $\text{CH}_3\text{Mn}(\text{CO})_5$ altogether. It was deduced from these results that the critical component is not CO, but CH_3 , whose availability controls the reaction. The ubiquitousness of $\text{Mn}_2(\text{CO})_{10}$ is somewhat surprising, since its formation must, at some stage, involve a bimolecular reaction. More unexpected is the high yield of the "dimeric" fulvalene $\text{Mn}_2(\text{CO})_6$, where Narayan's axiom (above) would suggest a low yield of such a complicated molecule.

Recent work on $[\text{CpFe}(\text{CO})_2]_2$ was intended to test whether once again a complex molecule could be found to have a high yield and also to test a possible preferential formation of metal carbonyls over metal sandwich compounds. In this compound, thermal decomposition of the starting compound gives rise predominantly to ferrocene (28, 68). The data (50) given in Table VIII show that indeed the carbonyl is preferentially formed

TABLE VIII
RADIOCHEMICAL YIELDS IN NEUTRON-IRRADIATED $[\text{CpFe}(\text{CO})_2]_2^a$

Target	Product	Y_{25} (%)	Y_{75}^{15} (%)
$[\text{CpFe}(\text{CO})_2]_2$	$\text{Fe}(\text{CO})_5$	3.2	5.4
	$[\text{CpFe}(\text{CO})_2]_2$	15.9	20.1
	FeCp_2	1.4	1.4

^a Y_T^t gives the yield after t minutes at $T^\circ\text{C}$. Samples were irradiated in Dry Ice. From Kanellakopulos-Drossopulos and Wiles (50).

but that, in this case, the preference seems to be exerted partly through thermal reactions, while the FeCp_2 is formed by prethermal reactions. Once again the yield of the parent is quite high. The annealing behavior was also

interesting, being an approximately linear function of temperature for isochronal treatment.

In addition to these studies, Baumgärtner *et al.* (8) were able to prepare, for the first time, tracer quantities of $\text{CpTc}(\text{CO})_3$ by β -decay of $[\text{Cp}^{99}\text{Mo}(\text{CO})_3]_2$. No search was made, however, for other product compounds.

Through these experiments run a few tenuous threads of consistency. There seems in all cases to be a reasonably good yield of the metal carbonyl (or of monomeric derivatives) and less of the two-ring sandwich. The mechanisms for this selectivity are not known and need not be the same for all compounds. Indications are that radical reactions play a dominant role in both the thermal and prethermal reactions, although conclusive proof is still lacking. From the $[\text{CpFe}(\text{CO})_2]_2$ work comes the conclusion that the Cp groups are added to the Fe only through prethermal reactions, while the carbonyls can also be added later through thermal reactions. There is not yet enough evidence to support this as a general principle, although data from many other systems are consistent with thermal reaction of CO. In several cases it has been found that hitherto unidentified compounds have been produced—sometimes in good yields—both by thermal and by prethermal reactions.

The only other mixed compounds which have been studied are Cp_2HfCl_2 and Cp_2ZrCl_2 (38), $\text{RMn}(\text{CO})_5$ (42), and $\text{XMn}(\text{CO})_5$ (48). Quite high yields were found for Cp_2HfCl_2 and Cp_2ZrCl_2 , with strong isotope effects (yields are 59.7% and 20.7%, respectively, for $\text{Cp}_2^{180\text{m}}\text{HfCl}_2$ and $\text{Cp}_2^{181}\text{HfCl}_2$). Analogous isotope effects were found in solution and also with 14 MeV neutrons. It was argued that the yield values could be separated into additive contributions from primary retention, primary recombination, and displacement reactions. The primary retentions, as determined from irradiation in solution, were much higher than Zahn's for $\text{Mn}_2(\text{CO})_{10}$ and were claimed to be 25% for $\text{Cp}_2^{180\text{m}}\text{HfCl}_2$.

The data for $\text{RMn}(\text{CO})_5$ ($\text{R} = \text{H}, \text{D}, \text{CH}_3, \text{C}_6\text{H}_5$) are given (42) in Table IX. Most interesting is the fact that the yields of $\text{HMn}(\text{CO})_5$ are in no way proportional to the number of hydrogen atoms in the target molecule. Subsequent results (41) have shown that the hydrogen (and deuterium) in $\text{HMn}(\text{CO})_5$ and $\text{DMn}(\text{CO})_5$ are quite labile. The values given in Table IX for these two compounds are thus not necessarily true recoil yields since they can well come from simple exchange reactions. This suggests that the $-\text{Mn}(\text{CO})_5$ group, at least, is formed in high yield before the time of the

TABLE IX
YIELDS IN RMn(CO)_5 , WITH NO THERMAL
TREATMENT^a

Target	Parent yield	HMn(CO)_5 yield
HMn(CO)_5		21.0
DMn(CO)_5		23.6
$\text{CH}_3\text{Mn(CO)}_5$	3.5	6.9
$\text{C}_6\text{H}_5\text{Mn(CO)}_5$	2.5	2.1

^a From Jakubinek *et al.* (42).

exchange. An isotope effect would not be expected in such cases, since by Harbottle's principle (29) any such effect would be swamped by the exchange.

TABLE X
YIELDS IN XMn(CO)_5 , WITH ANNEALING^a

Product	Target			
	IMn(CO)_5 (%)		BrMn(CO)_5 (%)	
$^*\text{XMn(CO)}_5$	28.5	47	49	62
$\text{X}^*\text{Mn(CO)}_5$	10.3	12	6.5	6.5
$[\text{X}^*\text{Mn(CO)}_4]_2$	—	—	28	30
$[\text{X}^*\text{Mn(CO)}_4]_2$	1.7	~0.5	2.0	1
$\text{Mn}_2(\text{CO})_{10}$	3.0	~3	1.9	1.7

^a The first number given in each case is the room-temperature yield, while the second is the yield after 6 minutes at 70° C. From de Jong and Wiles (48).

The XMn(CO)_5 system (48) is represented in Table X. Here it was concluded that the last step in formation of $^*\text{IMn(CO)}_5$ is addition of a carbonyl, while in the formation of $\text{I}^*\text{Mn(CO)}_5$ the last step seems to be addition of iodine.

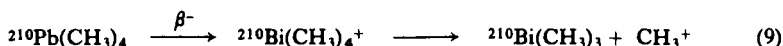
C. The Effects of β -Decay²

1. Chemical Changes

The process of β -decay in some respects offers simpler radiochemical consequences than do neutron capture and other reactions, because (a) the nuclear recoil energy is very low and (b) the decay schemes, and thus the probability of Auger cascades, are generally well known. Despite this, no clear mechanisms have been worked out.

The best-studied system is $\text{Pb}(\text{CH}_3)_4$. This can easily be prepared using 22-yr ^{210}Pb , which decays to ^{210}Bi by branched β -emission—maximum β -energies 15 keV (81%) and 61 keV (19%). The crossover γ -transition is 14% converted. The results of various studies (22, 21) show retention of bonding in some 70–80% of the ^{210}Bi formed in the gas phase, and a similarly high yield in dilute solutions. Curiously, the yield of $^{210}\text{Bi}(\text{CH}_3)_4$ fell to 18% at a mole fraction of 0.05 and rose again on further dilution (21). Adloff (2) has studied the β decay of $^{210}\text{PbPh}_4$, with comparable results.

Recognizing that the maximum recoil energy is about 0.04 eV, we see that the molecule must be preserved intact in most instances, to dissociate subsequently.



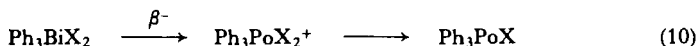
Loss of a CH_3^+ ion was found (21) to be some 110 kcal mole⁻¹ more favorable than dissociation to give a methyl radical.

On the basis of experimental data, Snell (78) has suggested that about one-fifth of the atoms following β -decay are likely to lose several electrons by “shakeoff,” and thus likely suffer dissociation of their molecules. The remaining four-fifths of the molecules may remain intact. (This principle is called the “four-fifths rule.”) Considering this and the 14% conversion of the γ -ray, one expects 69% of the $^{210}\text{Bi}(\text{CH}_3)_4$ to be preserved—fairly close to the value 70% found for dilute solutions. This may lend support to the frequent contention that bond breakage is the result of Auger ionization. (There are reasons for doubting this in condensed states, but unfortunately, data on fast intermolecular electron transfer are lacking.)

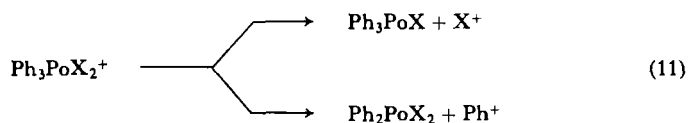
The decay of ^{210}Bi to ^{210}Po was studied in the phenylbismuth halides— Ph_3BiX_2 —by Nefedov and his colleagues (65). In this case, no γ -ray

² The author gratefully acknowledges the collaboration of Professor F. Baumgärtner in preparing this section.

transition occurs, so that Auger ionization can have no effect. The calculated maximum recoil energy from the β^- -emission is 3.5 eV, and the average recoil energy substantially less. Through a reaction sequence claimed to be



the observed yields of Ph_3PoX are, for $\text{X} = \text{Br}$, Cl , and F , 73%, 33%, and 5%, respectively. The formation of Ph_2PoX_2 showed the opposite trends. These yields must clearly reflect the effect of the halogen's electronegativities on the reactions



the second alternative being favored by higher electronegativity.

The several cases reported of very high yields of nuclear fission products in molecule form clearly involve preservation of bonds formed by β -precursors. These and a number of other studies will be discussed in the next section.

2. β -Decay as a Method of Synthesis

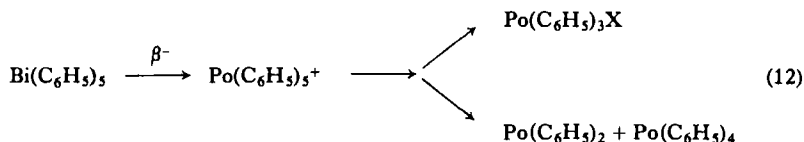
β -Decay is not only suited for mechanistic studies, but also offers to pure chemistry a means of answering the questions of the existence of unknown molecules. Failure to observe a particular compound in the systematics of organometallic chemistry can have several causes. Commonly it is because either an insufficient amount of the starting element is available (because it is too unstable or too difficult to obtain) or the selected preparative methods were unsuccessful. False methods in preparative attempts are not, however, good evidence for the nonexistence of a compound, but show as a rule only that the desired structure cannot be *reached* by a chosen pathway. β -Decay, on the other hand, starts from the point of having a neighboring element already in the desired structure. After β -decay, one seeks to find the decay product having *retained* its structure. This method, of course, presupposes that the desired structure is known for the neighbor element. Moreover, in order that the extremely small quantities of the product compound can be detected, it is necessary that the product nucleus must itself be radioactive, and that an Auger cascade not be associated with each decay event (as is increasingly the case with increasing atomic number). Corresponding to

these conditions, previously unknown organometallic compounds of Pm, Tc, Rh, Po, and Np have for the first time been synthesized and studied.

In the chemistry of cyclopentadienyl-metal complexes the question was always present as to whether the uncharged compound $\text{Rh}(\text{C}_5\text{H}_5)_2$ was capable of existence since the very stable compounds $\text{Fe}(\text{C}_5\text{H}_5)_2$, $\text{Co}(\text{C}_5\text{H}_5)_2^+$, $\text{Ru}(\text{C}_5\text{H}_5)_2$, and $\text{Rh}(\text{C}_5\text{H}_5)_2^+$ were known. The uncharged $\text{Co}(\text{C}_5\text{H}_5)_2$ showed a very high sensitivity to oxidation, so that the existence of the homologous Rh compound was already in question. The mass 105 decay series was especially suited for answering this question (7). The β^- -active ($t_{1/2} = 4.5$ hours) starting molecule $^{105}\text{Ru}(\text{C}_5\text{H}_5)_2$ could be easily prepared by neutron irradiation of natural $\text{Ru}(\text{C}_5\text{H}_5)_2$ followed by purification by sublimation. After the β -transformation, the criterion adopted for demonstrating the presence of the desired product compound was the volatility of the ^{105}Rh activity at 120°C . In fact, 15–20% of the ^{105}Rh present was found to be sublimable (7). Subsequent attempts to synthesize the volatile Rh compound chemically led to $\text{Rh}(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_6)$.

In a similar manner, the existence of $(\text{C}_5\text{H}_5)\text{Tc}(\text{CO})_3$ (9) and of $\text{Tc}(\text{C}_5\text{H}_5)_2^+$ (8) was demonstrated for the first time, starting from corresponding organometallic compounds of ^{99}Mo , which undergoes β^- -decay to $^{99\text{m}}\text{Tc}$. These compounds were also subsequently synthesized, and the chemical properties found following radiochemical synthesis were confirmed. Among the cyclopentadienyl lanthanide compounds, $\text{Pm}(\text{C}_5\text{H}_5)_3$ was first prepared by the β^- -decay of $^{151}\text{Nd}(\text{C}_5\text{H}_5)_3$ (6).

$\text{Po}(\text{C}_6\text{H}_5)_3\text{X}$, $\text{Po}(\text{C}_6\text{H}_5)_2$, and $\text{Po}(\text{C}_6\text{H}_5)_4$ were also first prepared by β -decay (63):

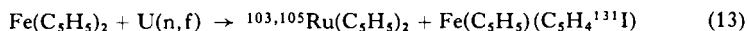


The di- and tetraphenylpolonium could not be distinguished by the paper chromatographic method used, as was also found with $\text{Te}(\text{C}_6\text{H}_5)_4$ and $\text{Te}(\text{C}_6\text{H}_5)_2$, produced by decay of $^{125}\text{Sb}(\text{C}_6\text{H}_5)_3$. The polonium-210 synthesis starting with $\text{Bi}(\text{C}_6\text{H}_5)_3$ or $\text{Bi}(\text{C}_6\text{H}_5)\text{Cl}_2$ (60) produced only $\text{Po}(\text{C}_6\text{H}_5)_3\text{Cl}_2$, and gave no trace of $\text{Po}(\text{C}_6\text{H}_5)_3$.

The existence and properties of $\text{Np}(\text{C}_5\text{H}_5)_3\text{Cl}$ were first determined (5) by β -decay synthesis. $^{238}\text{U}(\text{C}_5\text{H}_5)_3\text{Cl}$ served as the starting compound, being first converted by neutron irradiation to β^- -active $^{239}\text{U}(\text{C}_5\text{H}_5)_3\text{Cl}$. Since the

β -decay involves only a single, unconverted γ -ray, one should expect a high yield. The yield of the volatile Np compound was found to be 90%.

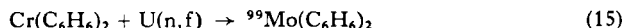
In connection with β -decay synthesis, the synthesis of organometallic compounds as a consequence of nuclear fission must be mentioned (9-11, 13). In this way, for example, a powdered mixture of $\text{Fe}(\text{C}_5\text{H}_5)_2$ and U_3O_8 gives good yields of ruthenocene (10) and iodoferrocene (9) on fission.



Similarly, by neutron irradiation of a mixture of U_3O_8 and $\text{Cr}(\text{CO})_6$, one gets the homologous compound ${}^{99}\text{Mo}(\text{CO})_6$ (11):



Chemically very sensitive compounds, such as the easily oxidizable $\text{Mo}(\text{C}_6\text{H}_6)_2$, are formed when air is excluded.



The high yields—about 50%—which were observed in all cases, indicate the strong involvement of secondary fission products (i.e., those produced by β -decay of precursors). A consideration of mechanisms of formation of the organometallic products led to the conclusion (13) that the β -decay itself must be the cause of the molecule formation. Neither purely mechanical collisional substitution, nor thermal chemical reactions, nor radical reactions, nor radiation-induced reactions seemed to be responsible for the synthesis reactions.

IV

DISCUSSION

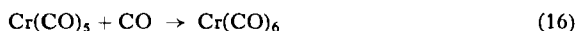
A. Reaction Mechanisms

Any attempted discussion of reaction mechanisms in this present context must present a rather disappointing picture. Although numerous plausible hypotheses have been advanced, it may fairly be said that practically nothing is known with certainty regarding the mechanisms of the inferred reactions. The best which can be done at present—and this only in a few cases—is to identify the approximate time of occurrence of the reactions. Unfortunately this is not as easily done in solids as in liquids or gases where scavengers or moderators can be used during or after the irradiation. Nonetheless some progress can be made which, if it does not elucidate the mechanism, at least

suggests areas for focusing of future research. We now examine the possible stages for the occurrence of the reactions, and some of the principles which have been used, explicitly or implicitly, to evaluate the contribution of each to the final spectrum of products.

1. *Thermal Reactions*

Thermal reactions are the easiest to isolate experimentally, although they are seldom easy to identify precisely. Clearly, any compound whose yield is influenced by thermal treatment involves, in part at least, thermal reactions. These thermal reactions can be of two types: those which lead to the addition of further ligands, and those which do not. Only the first type are commonly considered and involve addition of a ligand to complete the molecule to give an identifiable intermediate:



Thermal reactions of the second type, which do not involve adding ligands toward formation of metal organic product compounds, are less widely recognized as chemical phenomena. There may be here a simple failure of reaction, as in Eq. (16), because (99) of the diffusion of CO from the reaction site; there may be stabilization of an intermediate stage by scavenger action (26, 27, 56):



or there may be, at increased temperature, thermal dissociation of an intermediate product (44).



These are all envisioned as occurring in the solid state.

Failure to give a product because of diffusion away of a reactant may give rise to kinetic competition between two processes: reaction with activation energy E_1 and diffusion with activation energy E_2 . This competition can easily be handled using assumed first-order kinetics (for correlated pairs of reactants) and considering the fraction, F , of the available reaction sites which lead to products within "infinite" time compared to the fraction, $1 - F$, which give no reaction—presumably by diffusion away of a reactant. This treatment leads to the expression

$$F = \frac{R_T^\infty}{R^0} = \frac{k_1 \exp(-E_1/kT)}{k_1 \exp(-E_1/kT) + k_2 \exp(-E_2/kT)} \quad (20)$$

which leads to retention values at the annealing plateau of

$$\log R_T^\infty = \log \left(R^0 \frac{k_1}{k_2} \right) - \frac{E_1 - E_2}{k} \frac{1}{T} \quad (21)$$

The linear relationship given in Eq. (21) between $\log R$ and $1/T$ has been observed in ionic compounds with K_2CrO_4 (55) and KIO_3 (17), but not yet with organometallic compounds. The work of Zahn *et al.* (99) suggests that such a relationship may exist, but the data are too few as yet.

The nature of the first type of thermal reactions is as yet only speculative. The two obvious possibilities seem to be (1) reaction of an incomplete molecule (radical) with an unbound nearby ligand, made available by recoil fragmentation, radiolysis, chemical dissociation, or the presence of an external atmosphere and (2) reaction of the moiety with a nearby molecule to abstract a ligand. The first type with an external source of CO has been clearly demonstrated for the case of the Group VI carbonyls which, when heated in an atmosphere of CO (up to 100 atm pressure) showed a marked increase in yield. A much smaller enhancement of yield *in vacuo* was attributed (99) to radiolytic dissociation, because of the influence of irradiation at various γ -fluxes. The alternative possibility—that of equilibrium dissociation of $Cr(CO)_6$ in the solid state—has not been investigated.

Other probable cases of addition of CO to complete a molecule by thermal reactions are $Mo(CO)_6$ (99), $W(CO)_6$ (61, 99) $[CpFe(CO)_2]_2$ (50), $Fe(CO)_5$ in $[CpFe(CO)_2]_2$ (50), $*IMn(CO)_5$ (48), and $Ni(CO)_4$ (92). This last seems to show the importance of normal thermal dissociation, although radiolytic effects have not been ruled out. Most other ligands which have been studied have, on one compound or another, been found to be capable of thermal reaction—Ph in $AsPh_3$, CO in several compounds, I and Br in $XMn(CO)_5$, Cp in $FeCp_2$, PhH in $Cr(PhH)_2$. Many of these same ligands have also been found to react prethermally in other cases.

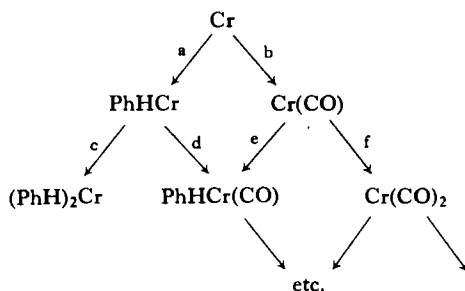
Implicit in all this discussion of thermal reactions is the requirement that the moiety be stable enough in the solid state to last until reacting. The IR spectra of such partial molecules and their reactions have been observed for several cases. Rest and Turner (71) have shown that at 15° K the fragment $Ni(CO)_3$ is stable enough in an argon matrix to adopt its own characteristic symmetry (D_{3h}). Reformation of the whole molecule occurs rapidly at 30° K. Similarly (70), $Mn(CO)_3NO$ and $Mn(CO)_2NO$ are stable in an argon matrix at 15° K and react to form $Mn(CO)_4NO$ at 30° K. In these cases, the fragmentation was induced photolytically so the dissociation products likely

remained at those temperatures in a reactive configuration. There is no information as to the stabilities of these moieties in the absence of a stabilizing reaction. The evident stability of $\cdot\text{Mn}(\text{CO})_5$ in $\text{Mn}_2(\text{CO})_{10}$ at temperatures up to 50°C has already been discussed (44).

Little evidence for thermal transfer of a π -ring in recoil studies has been published, and that only when no other ligand was present in the molecule. It is found (85, 37) that ferrocene is susceptible to thermal annealing in a ferrocene matrix, where the reaction clearly must be

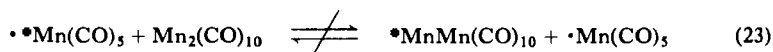


On the other hand, the yield of ferrocene in a $[\text{CpFe}(\text{CO})_2]_2$ matrix (50) is not altered up to 80°C , so that here either Cp transfer is not possible or the position on the Fe atom is blocked by CO groups. It seems plausible to consider a rapid "ligand condensation" as a very early prethermal competitive reaction. One can thus set up a hypothetical reaction scheme such as [using $\text{PhHCr}(\text{CO})_3$ as the matrix compound]:



Either reaction b or reaction d would preclude subsequent formation of $(\text{PhH})_2\text{Cr}$. After the initial period of chemical and thermal excitation, the CO would enjoy a strong kinetic advantage over the ring, both because of its small size and because of its favorable π -electron distribution, so that reaction d would be preferred over c, and f would be preferred over e.

Also interesting chemically is the identification of some expected reactions which do not occur in the solid state (45). Among these is the exchange of $\cdot\text{Mn}(\text{CO})_5$ with an $\text{Mn}_2(\text{CO})_{10}$ matrix.



This reaction is not detectable within 6 minutes at 75°C (44).

It is evident that much more work is needed on the stability and reactivity

of radicals trapped in solids and on the mobility of unbound ligands in solids. The occurrence of thermal reactions in solid irradiated samples is now well documented, and it can be deduced what reactions are probably occurring. However, little more can be said now, until more quantitative data are available on mobilities and activation energies.

2. Separation-Induced Reactions

Radioactive molecules can sometimes be formed by the processes normally involved in the separation. Foremost among these are (1) exchange in the solvent prior to chromatography and (2) thermal reaction during sublimation. Both lead to false results; the second is easily eliminated, the first is often not. As an illustration of the effect of sublimation, it was found (61) that the yield of $^{186}\text{W}(\text{CO})_6$ separated by vacuum sublimation at 50°C was 63.8%. The same irradiation conditions yielded 51.8% when the samples were first chromatographed and then sublimed. Evidence for similar effects was found in $(\text{PhH})_2\text{Cr}$ (15), RuCp_2 (29) and others. Simple dissolution to break up the lattice, followed by evaporation and sublimation is usually considered satisfactory to eliminate thermal recombination of initially correlated pairs of reactants.

Exchange in solution is not so easy to identify, although dissolution in scavenger solutions has proven satisfactory in several cases. Often, once the problem has been recognized, little more can be done about it, as in the case of the yield of $^*\text{MnCp}_2$ in $\text{CpMn}(\text{CO})_3$. By direct experiment this yield was found (80) to be 60%—a surprisingly high value. However, the same experiment done on irradiated $\text{Mn}_2(\text{CO})_{10}$ showed a yield of about 30%. Clearly in the latter case the MnCp_2 carrier exchanges with some radioactive species in the solution. Since the amounts of carrier and tracer differ so greatly, the equilibrium position will be so far in the direction of the radioactive carrier that the reaction is effectively unidirectional.

Exchange reactions can sometimes be used to good advantage when carriers do not exist. The radical $\cdot\text{Mn}(\text{CO})_5$ is found to exchange rapidly with $\text{IMn}(\text{CO})_5$, which can then be used as carrier for the erstwhile radical. Information is lost by this exchange and the yields of pairs such as $\cdot\text{Mn}(\text{CO})_5$ and $\text{IMn}(\text{CO})_5$, $\text{HMn}(\text{CO})_5$ and $\text{IMn}(\text{CO})_5$, and FeCp_2 and FeCp_2^+ cannot be distinguished. A further problem here is that one must assume that the exchange is complete, so that the chemical recovery properly represents the radiochemical recovery. While it is possible that future developments may make it possible to use these exchange reactions more frequently

in identifying radioactive species, at the present it seems that little further information can be gathered from experiments involving rapid exchange. Conversely, it is possible that the radiochemical studies can lead to information about exchange kinetics; the above-mentioned MnCp_2 exchange is an example. However, no study of these reactions has been done and, of course, there is no certainty that they are in fact true exchange reactions.

3. *Prethermal Molecule Formation*

An observed product which is not formed by thermal or separation-induced reactions, or molecule fragments which may be recognized as reacting further at later stages, must be considered as being formed by prethermal reaction. Under this term we include reaction by direct collision, "hot zone" reactions, and epithermal reactions, but not thermal reactions occurring during the neutron irradiation. These last can usually be identified or eliminated by irradiating at different, low temperatures. It is a useful, if not fully tested, principle that an identified species whose yield is not affected by thermal treatment or by changes in separation procedure or in irradiation conditions must have been formed by prethermal reactions. Species which remain after partial or total failure of bond rupture will be discussed below, and can likely not be distinguished in practice.

The only case reported to date in which prethermal reactions seem to be the sole means of formation is that of ferrocene, formed in 1.4% yield in $[\text{CpFe}(\text{CO})_2]_2$. While exhaustive study of the effects of irradiation conditions was not made, thermal annealing had no effect on the FeCp_2 yield, and no difference was found between irradiation at -78°C at $3 \times 10^{11} \text{ n cm}^{-2} \text{ sec}^{-1}$ and at 35° at $9 \times 10^{13} \text{ n cm}^{-2} \text{ sec}^{-1}$. Other products were markedly affected by these same changes of experimental conditions. Thermal and radiation effects on the parent yields in RuCp_2 are very small, and isotope effects are large (29). This suggests, in accord with Harbottle's axiom (see below), that most of the RuCp_2 is prethermally formed. The parent yield in $\text{Mn}_2(\text{CO})_{10}$ seems to be independent of thermal treatment and of dissolution medium, but the irradiation conditions have not been studied over a wide enough range to permit exclusion of γ -radiation effects as a contributing factor. All other reported cases show evidence of formation at least partially by later reactions.

While inference has been made in a few cases as to the order of addition of ligands in prethermal reactions, no generalization can yet be made. When only one type of ligand is present, it is clear that the same ligand type may

react both prethermally and thermally. In liquid systems it is possible to intercept the thermal reactions by the use of scavengers, or to further them by the use of additional radical sources (44). It is also possible to intercept some of the prethermal reactions by the use of large concentrations of scavengers. In this way Siekierska *et al.* (76) were able to determine the upper limits on various stages of the reactions in benzene solutions of AsPh_3 , as is seen in Table XI.

TABLE XI
CONTRIBUTION FROM PROCESSES AT VARIOUS STAGES IN THE
TRIPHENYLARSINE BENZENE SYSTEM^a

	Percent ^{76}As as		
	AsPh_3	$-\text{AsPh}_2$	$=\text{AsPh}$
Failure of bond rupture	1-2	2	0
Hot reactions	1	5	22 ^b
Thermal reactions	14	16	0

^a Data from Siekierska *et al.* (75).

^b Some 6% of this is susceptible to further thermal reaction with phenyl groups unless "scavenged" by oxygen to form $\text{PhAsO}(\text{OH})_2$.

When two or more types of ligand are present, it often appears that one takes precedence over the other. Thus, with $[\text{CpFe}(\text{CO})_2]_2$ it appears that the Fe-Cp bonds are made either very fast or not at all, and that any thermal effects involve the making of Fe-CO bonds. It may well be that the FeCp fragment is not stable enough to last through the prethermal period and rapidly adds either Cp to give FeCp_2 , or CO which permanently blocks the access of a second Cp, much as was suggested above for $\text{PhHCr}(\text{CO})_3$. If this suggestion is valid for $\text{CpMn}(\text{CO})_3$, the blocking seems not to be permanent, as is shown by the evident rapid exchange with MnCp_2 carrier.

The difficulty in proving the exact nature of prethermal reactions is that they occur too fast for standard solid-state chemical methods. One attractive idea was expressed by Harbottle (29), namely that, if a strong isotope effect is shown, very little subsequent chemical influence can have been felt and the observed species must have been formed by prethermal processes. The supposition here is that isotopic differences come only from differences in the nuclear deexcitation pattern (total energy, γ -ray cascades, angular

correlation, conversion coefficients, etc.) and that subsequent thermal reactions will have no tendency to preserve memory of the nuclear event. While this hypothesis has not been examined further, it seems promising and deserves more attention. Harbottle's initial statement was that the greatest isotope effects are given in experimental conditions which lead to the lowest yields. Since most, if not all, annealing effects lead to increased yields, the other formulation of the axiom follows. Harbottle's data are given in Section III,B,2.

4. *Failure of Bond Rupture*

Failure of bond rupture presents an unsolved question which has not been well discussed. This may be particularly significant in cases of certain complex molecules which, despite their complexity, seem to show high yields. If, as in the case of $[\text{CpFe}(\text{CO})_2]_2$, the direction of recoil were to be toward the center of mass of the molecule, it is likely that a large amount of the energy could be absorbed within the molecule, at least long enough for the atoms to remain in essentially their normal configurations while the energy is transferred to neighboring molecules. If we allow for emission of a small number of medium energy γ -rays, with probable partial momentum cancellation, it is apparent that at least some of the bonds must remain intact in a substantial fraction of the events. It is thus tempting to speculate that this partial preservation of structure may be the reason for the high yields observed for several complex compounds.

A similar explanation may be useful in interpreting the apparent preference for one ligand over another, because of the particular orientation of the molecules in the crystals. $\text{CpMn}(\text{CO})_3$ molecules, for example, are arranged approximately as shown in Fig. 4 (16). The recoiling atom can escape in several directions, including through the carbonyl umbrella. This is very much like the mechanism proposed (84) for exchange of PhH with $\text{PhHCr}(\text{CO})_3$, and would leave the Mn atom surrounded entirely by carbonyls. Recoil in the opposite direction is not possible without destroying the ring (93). This speculation will be very difficult to test by direct experiment, although a promising approach will be that of ion implantation chemistry, in which the chemical form of radioactive atoms shot into various targets can be compared with the product spectrum of atoms formed by neutron activation in similar compounds.

To counter the suggestion that bond preservation may be required, there are several cases of efficient formation of radioactive molecules where no

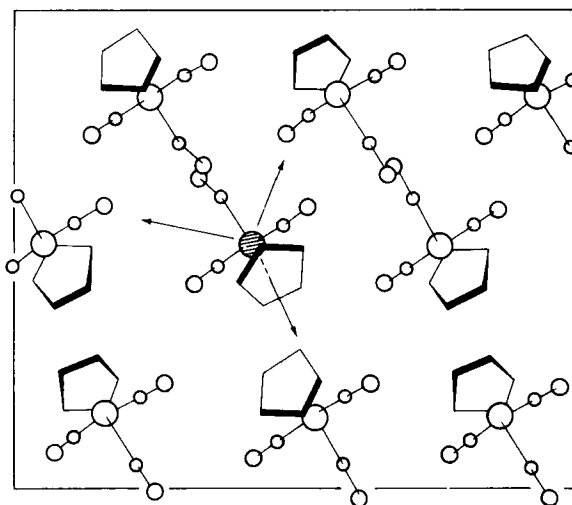


FIG. 4. Crystal structure of CpMn(CO)_3 [after ref. (16)] showing recoil into CO-rich regions and recoil into a Cp-rich region. Destruction of the initial ligand Cp occurs in this last event.

bond was formerly present. These include the experiments of Henrich and Wolf (34) and of Harbottle and Zahn (30) on high-energy bombardment of metal carbonyls and the work by Zahn and Harbottle (100) and by Baumgärtner and co-workers (4, 9, 11–13) on capturing fission fragments in an appropriate catcher material. For example, when a finely ground mixture of U_3O_8 and Cr(CO)_6 was irradiated with neutrons, up to 60% of the ^{99}Mo was found (11) as Mo(CO)_6 .

Another case in which bonds were made where none existed previously is that of irradiation of AsCl_3 in benzene solution (76) which led to formation of PhAsCl_2 and Ph_2AsCl , and even Ph_3As . Yet another example (51) is the formation of $^{59}\text{FeCp}_2$ by irradiation of Fe(CO)_5 in cyclopentadiene (monomer) solution. While these examples may not tell us when the reaction does occur, they do show that initial bonding is not indispensable.

5. "Nonproductive" Reactions

We have so far concentrated on those reactions which can lead to recognizable product species. In most cases, however, an appreciable fraction of the radioactive atoms are in chemical forms which are not identified until they ultimately emerge as metal ions in aqueous acid solution. Although the term

“inorganic fraction” has been used, it is likely that these atoms may be in more complex, perhaps metastable, forms. Are there, then, other reactions or conditions whose effect is specifically to prevent the formation of molecular products? There are few conclusive data but much indicative evidence. There seem to be two general types of reactions here, although proper classification has not been attempted:

- (1) Irreversible destruction in the nuclear event
- (2) Scavenging of radicals and incomplete molecules

As early as 1940, Seaborg *et al.* (74) pointed out a close relationship between the radiochemical yield and the conversion coefficient of a nuclear isomeric transition. Studying $\text{Te}(\text{C}_2\text{H}_5)_2$ and $\text{Zn}(\text{C}_2\text{H}_5)_2$, they concluded that the molecules were permanently destroyed by the results of subsequent internal conversion. Briefly, they found in the gaseous compounds $\text{M}(\text{C}_2\text{H}_5)_2$ that for $\text{M} = {}^{127}\text{Te}^m$ and ${}^{129}\text{Te}^m$, which are almost totally converted, the radioactive ground state species ${}^{127}\text{Te}$ and ${}^{129}\text{Te}$ were 100% transformed to non-volatile decomposition products. For the largely unconverted ${}^{69}\text{Zn}^m$, on the other hand, no such decomposition was observed.

Similar suggestions have been made in several other cases (34, 57, 64, 72). Often, however, the evidence is incomplete so that other interpretations cannot be ruled out. The important and convincing work of Carlson and White (18) on $\text{Pb}(\text{CH}_3)_4$ has already been described. However, its applicability to the condensed states has not been studied.

The importance of scavengers has been referred to earlier, but destructive scavenging action is much more widespread—for the obvious reason that the products are seldom recoverable. In addition to scavengers which are added intentionally to remove contaminants in known species, scavenger action is present through accidental or unavoidable presence of air or moisture in chromatography solvents. The clearest example of this is perhaps the formation of oxygenated species from Ph_3As , recognized by Maddock and Sutin as products of radical scavenging reactions (56). Radiation-produced scavenger action was pointed out by Nowak and Akerman (67) as responsible for the decrease in yields of certain products—particularly vinyl compounds—from $\text{Ge}(\text{C}_2\text{H}_5)_4$ at higher radiation intensities.

Less clearly recognizable as scavenging, but in principle the same thing, is the evident reaction of glass surfaces with carrier-free species. While this phenomenon has been studied widely in radiochemistry, adsorption on the walls of glass vessels has been more of a nuisance to be avoided. Harbottle

and Zahn (29) have shown that these adsorbed species can react chemically to form molecules—in their case RuCp_2 from initially ionic ruthenium. An interesting case is the adsorption of some 30% of the radioactive ^{59}Fe from FeCp_2 on the walls of the vessels used for dissolution (85). This was not a species produced by hydrolysis and was best removed by washing the glass with acetone. It would be very interesting to try to scavenge this species before it reached the walls, so as to make an identification. It seems possible that it may be FeCp , which could perhaps be captured by further reaction with monomeric Cp .

In the case of many target compounds this unrecovered fraction, erroneously called the “inorganic” fraction, must remain unidentified until more work can be done on the use of scavengers to intercept and protect partly formed molecules.

B. Applications to Other Fields

The only respect in which the hot atom chemistry of organometallic compounds has so far been applied to other fields of study is in the area of isotope enrichment. Much of this has been done for isolation of radioactive nuclides from other radioactive species for the purpose of nuclear chemical study, or for the preparation of high specific activity radioactive tracers. Some examples of these applications have been given in Table II. The most serious difficulty with preparation of carrier-free tracers by this method is that of radiolysis of the target compound, which can be severe under conditions suited to commercial isotope production, so that the radiolysis products dilute the enriched isotopes. A balance can be struck in some cases, however, between high yield and high specific activity (19, 73).

Formation of labeled molecules has been studied in a few cases, but has not been exploited usefully. Various radioactive organomercury compounds have been prepared: diphenylmercury (33, 90), fluorescein (53), and chloromeredrin (43). A number of other potentially useful syntheses could doubtless be developed with a wide variety of nuclides with easily detectable γ -rays—pharmaceuticals, pesticides, physiological tracers, oil-soluble markers for labeling oil shipments, and so on—if it could be established what molecules are of interest to the various “consumers”

Applications to the study of the chemical properties of the compounds concerned have been only little explored, and to date the work has essentially just begun with a couple of reports on manganese compounds. Potential

uses lie in studies (45) of the exchange of otherwise inaccessible radicals or of "foreign" compounds in solids, produced *in situ*, or of unstable species which can be frozen in solid matrices to react rapidly on dissolution. Another potential use is in the more conventional studies of reaction kinetics (41, 42) in cases where the labeled molecule would be very difficult to synthesize by standard methods.

The use of β -decay as a synthetic route has been described earlier (Section III,C,2) and again has been exploited only little.

C. Future Trends

Over the past few years studies in this field of research have (perhaps rightly) been rather poorly correlated searches for phenomena which could often best serve as focus for seeking specific questions. Now some of these questions can be asked, and hopefully future work may be better coordinated. It is now possible to look for solutions to questions such as the following:

What are the starting species for the observed thermal reactions?

What is the role of selective bond rupture in determining the nature of the products?

What are the relative roles of kinetic recoil energy and of electronic effects in leading to the observed products?

What alternative routes are open for the dissipation of the energy of the capture γ -cascade?

At what stage do preferential reactions express themselves, and what are the parameters leading to this preference?

What chemical phenomena lead to the "inorganic" or nonmolecular products?

It is likely that the answers to these questions will come only from more selective and sophisticated experiments than have been done hitherto, although some useful directions have been established. The use of high-sensitivity electron spin resonance for the study *in situ* of anticipated radical species will likely be possible, if the background signals from other radiation-produced species are not too intense. Studies of the chemistry of implanted atoms and ions in solid organometallic substrates will make it possible to start with totally unbound atoms which suffer no Auger ionization and thus to simulate the extreme of the total recoil. Careful studies of the thermal annealing effects, especially in the presence of reactive atmospheres, will

help to determine the nature of the later reactions. Study of selected mixed alternative products will make possible the assessment of relative reaction probabilities. Mixed systems, such as $^{56}\text{FeCp}_2\text{--}^{58}\text{Fe}(\text{CO})_5$ (51) will be enlightening in so far as they may shed light on the thermal migration of the recoil atom. (In this case, it may rather be that the radiochemical studies will shed light on the phase composition of the frozen solutions.) Most interesting, but chemically difficult, would be the study of such binuclear compounds as the pair (49) $\text{Cp}_2\text{MoH}\cdot\text{W}(\text{CO})_5$ and $\text{Cp}_2\text{WH}\cdot\text{Mo}(\text{CO})_5$, to look for possible asymmetry in the distribution of $^{186}\text{W}(\text{CO})_6$ among the products.

NOTE ADDED IN PROOF

Recent experiments have provided partial answers to some of the above questions, although their generality is not yet known. Implantation of 4 keV $^{56}\text{Mn}^+$ ions into $\text{Cr}(\text{CO})_6$ targets does give rise to $-\text{}^{56}\text{Mn}(\text{CO})_4$ and $-\text{}^{56}\text{Mn}(\text{CO})_5$, but in quite low yield (<1%). (G. M. Jenkins and D. R. Wiles, to be published.) Generation of 18 keV ^{56}Mn in crystalline $[\text{CpFe}(\text{CO})_2]_2$ by the $^{56}\text{Fe}(n,p)^{56}\text{Mn}$ reaction produces very low yields of $\text{Cp}^{56}\text{Mn}(\text{CO})_3$ and $-\text{}^{56}\text{Mn}(\text{CO})_5$. (D. R. Wiles, to be published.) If the initiating species in the radiochemical reactions were a high energy recoil atom [cf. (i) in Fig. 2] then very high product yields would be expected in both of these cases.

GENERAL BIBLIOGRAPHY

- G1. "Chemical Effects of Nuclear Transformations," I.A.E.A. Symp., Vienna, 1961.
- G2. "Chemical Effects of Nuclear Transformations," I.A.E.A. Symp., Vienna, 1965.
- G3. Willard, J. E., *Annu. Rev. Nucl. Sci.* **3**, 193 (1953).
- G4. Harbottle, G., and Sutin, N., *Advan. Inorg. Chem. Radiochem.* **1**, 267 (1959).
- G5. Campbell, I. G., *Advan. Inorg. Chem. Radiochem.* **5**, 135 (1963).
- G6. Harbottle, G., *Annu. Rev. Nucl. Sci.* **15**, 89 (1965).
- G7. Müller, H., *Angew. Chem.* **79**, 128 (1967).
- G8. Siuda, A., Rev. Rep. No. 6 (Bibliography to 1962), Polish At. Energy Comm., Warsaw, 1963.
- G9. Adloff, J. P., Effets Chimiques des Transformations Nucléaires. Bibliography with annual supplements. Laboratoire de Chimie Nucléaire, Strasbourg (from 1963).
- G10. Stöcklin, G., "Chemie Heisser Atome." Verlag Chemie, Weinheim, 1969.

REFERENCES

- 1. Abouaf, R., *J. Phys. (Paris)* **31**, 277 (1970).
- 2. Adloff, M., and Adloff, J. P., *C.R. Acad. Sci.* **259**, 141 (1964).
- 3. Bartholomew, G. A., Doveika, A., Eastwood, K. M., Monaro, S., Groshev, L. V., Demidov, A. M., Pelekhov, V. I., and Sokolovskii, L. L., *Nucl. Data* **3**, 367 (1967).
- 4. Baumgärtner, F., see Ref. G2, Vol. 2, p. 507.

5. Baumgärtner, F., Fischer, E. O., and Laubereau, P., *Naturwissenschaften* **52**, 560 (1965).
6. Baumgärtner, F., Fischer, E. O., and Laubereau, P., *Radiochim. Acta* **7**, 188 (1967).
7. Baumgärtner, F., Fischer, E. O., and Zahn, U., *Chem. Ber.* **91**, 2336 (1958).
8. Baumgärtner, F., Fischer, E. O., and Zahn, U., *Naturwissenschaften* **49**, 156 (1962).
9. Baumgärtner, F. and Reichold, P., Ref. G1, Vol. II, p. 319.
10. Baumgärtner, F. and Reichold, P., *Z. Naturforsch. A* **16**, 374 (1961).
11. Baumgärtner, F. and Reichold, P., *Z. Naturforsch. A* **16**, 945 (1961).
12. Baumgärtner, F., and Schön, A., *Proc. Conf. Methods Preparing Storing Marked Molecules, Brussels, 1963*, p. 1331.
13. Baumgärtner, F., and Schön, A., *Radiochim. Acta* **3**, 141 (1964).
14. Baumgärtner, F., and Zahn, U., *Radiochim. Acta* **1**, 51 (1963).
15. Baumgärtner, F., Zahn, U., and Seeholzer, J., *Z. Naturforsch. A* **15**, 1806 (1960).
16. Berndt, A. F., and Marsh, R. E., *Acta Crystallogr.* **16**, 118 (1963).
17. Bjerkelund, K., Unpublished work, Carleton Univ., Ottawa, Canada.
18. Carlson, T. A., and White, R. M., *J. Chem. Phys.* **48**, 5191 (1968).
19. Colonomos, M., and Parker, W., *Radiochim. Acta* **12**, 163 (1969).
20. Costea, T., Negoescu, I., Vasudev, P., and Wiles, D. R., *Can. J. Chem.* **44**, 885 (1966).
21. Duncan, J. F., and Thomas, F. G., *J. Inorg. Nucl. Chem.* **29**, 869 (1967); see also Baulch, D., Duncan, J., and Thomas, F., Ref. G1, Vol. 2, p. 169.
22. Edwards, R. R., Day, J. M., and Overman, R. F., *J. Chem. Phys.* **21**, 1555 (1953).
23. Groening, H. R., and Harbottle, G., *Radiochim. Acta* **14**, 109 (1970).
24. Grossmann, G., *Isotopenpraxis* **5**, 262 (1969).
25. Grossmann, G., *Isotopenpraxis* **5**, 283 (1969).
26. Grossmann, G., *Isotopenpraxis* **5**, 370 (1969).
27. Grossmann, G., *Radiochim. Acta* **13**, 31 (1970).
28. Hallam, B. F., Mills, O. S., and Pauson, P. L., *J. Inorg. Nucl. Chem.* **1**, 313 (1955).
29. Harbottle, G. and Zahn, U., Ref. G2, Vol. II, p. 133.
30. Harbottle, G. and Zahn, U., *Radiochim. Acta* **8**, 114 (1967).
31. Heitz, C., *Bull. Soc. Chim. Fr.* 2439 (1967).
32. Heitz, C., *Bull. Soc. Chim. Fr.* 2442 (1967).
33. Heitz, C., and Adloff, J. P., *Bull. Soc. Chim. Fr.* 2917 (1964).
34. Henrich, E., and Wolf, G. K., in "The Uses of Cyclotrons in Chem. Metall. Biol." (C. B. Amphlett, ed.), p. 51. Butterworths, London, 1970; Rep. KFK 1067, Kernforschungszentrum Karlsruhe, 1969.
35. Herr, W., *Z. Naturforsch. B* **7**, 201 (1952).
36. Hillman, M., Kim, C. K., Shikata, E., and Weiss, A. J., *Radiochim. Acta* **9**, 212 (1968).
37. Hillman, M., and Weiss, A. J., Personal communication.
38. Hillman, M., Weiss, A. J., and Hahne, R. M. A., *Radiochim. Acta* **12**, 200 (1969).
39. Hsiung, C., Hsiung, H., and Gordus, A. A., *J. Chem. Phys.* **34**, 535 (1961).
40. Jach, J., and Sutin, N., *J. Inorg. Nucl. Chem.* **7**, 5 (1958).
41. Jakubinek, H., Unpublished work, Carleton Univ., Ottawa, Canada, 1971.
42. Jakubinek, H., Srinivasan, S. C., and Wiles, D. R., *Can. J. Chem.* **49**, 2175 (1971).
43. de Jong, I. G., Unpublished work, Carleton Univ., Ottawa, Canada.
44. de Jong, I. G., Srinivasan, S. C., and Wiles, D. R., *Can. J. Chem.* **47**, 1327 (1969).
45. de Jong, I. G., Srinivasan, S. C., and Wiles, D. R., *J. Organometal. Chem.* **26**, 119 (1971).
46. de Jong, I. G., and Wiles, D. R., *Chem. Commun.* 519 (1968).
47. de Jong, I. G., and Wiles, D. R., *Can. J. Chem.* **48**, 1614 (1970).
48. de Jong, I. G., and Wiles, D. R., *Can. J. Chem.* **50**, 961 (1972).
49. Kaesz, H. D., *J. Amer. Chem. Soc.* **90**, 3276 (1968).

50. Kanellakopulos-Drossopulos, W., and Wiles, D. R., *Can. J. Chem.* **49**, 2977 (1971).
51. Kanellakopulos-Drossopulos, W., and Wiles, D. R., *Radiochim. Acta* **16**, 179 (1971).
52. Kienle, P., Wien, K., Zahn, U., and Weckermann, B., *Z. Phys.* **176**, 226 (1963).
53. Kronrad, L., Ratusky, J., Malek, P., Vavrejn, B., and Kolc, J., *J. Label. Compounds* **6**, 326 (1970).
54. Libby, W. F., *J. Amer. Chem. Soc.* **69**, 2523 (1947).
55. Maddock, A. G., and de Maine, M. M., *Can. J. Chem.* **34**, 441 (1956).
56. Maddock, A. G., and Sutin, N., *Trans. Faraday Soc.* **51**, 184 (1955); *Research* **6**, Suppl., 78 (1953).
57. Merz, E., and Riedel, H. J., *Radiochim. Acta* **3**, 35 (1964).
58. Miller, J. M., Gryder, J. W., and Dodson, R. W., *J. Chem. Phys.* **18**, 579 (1950).
59. Mortenson, R. A., and Leighton, R. A., *J. Amer. Chem. Soc.* **56**, 2397 (1934).
60. Murin, A. N., Nefedov, V. D., Zaitsev, V. M., and Gracev, S. A., Ref. G1, Vol. 2, p. 183.
61. Narayan, S. R., and Wiles, D. R., *Can. J. Chem.* **47**, 1019 (1969).
62. Nath, A., Rao, K. A., and Thomas, V. G., *Radiochim. Acta* **3**, 134 (1964).
63. Nefedov, V. D., Shurawlev, M. A., Toropova, A. V., and Levshenko, A. V., *Radio-khimiya* **6**, 632 (1964).
64. Nefedov, V. D., Ryukhin, Yu. A., Toropova, M. A., Melnikov, V. N., and Chi-Minh, L., Ref. G2, Vol. 2, p. 149.
65. Nefedov, V. D., Vobecky, M., and Borak, J., *Radiochim. Acta* **4**, 104 (1965).
66. Nowak, M., *Int. J. Appl. Radiat. Isotop.* **16**, 649 (1965).
67. Nowak, M., and Akerman, K., *Radiochim. Acta* **13**, 48 (1970).
68. Piper, T. S., Cotton, F. A., and Wilkinson, G., *J. Inorg. Nucl. Chem.* **1**, 165 (1955).
69. Reichold, P., Ph.D. Dissertation, Munich, (1959).
70. Rest, A. J., *Chem. Commun.* 345 (1970).
71. Rest, A. J., and Turner, J. J., *Chem. Commun.* 1026 (1969).
72. Ross, R., Rep. ZfK-169, Zentral Inst. Kernforschung, Rossendorf bei Dresden 1969.
73. Schwartz, A., Rafaeloff, R., and Yellin, E., *Int. J. Appl. Radiat. Isotop.* **20**, 853 (1969).
74. Seaborg, G. T., Friedlander, G., and Kennedy, J. W., *J. Amer. Chem. Soc.* **62**, 1309 (1940).
75. Siekierska, K. E., Halpern, A., and Siuda, A., Ref. G1, Vol. I, p. 171.
76. Siekierska, K. E., and Sokolowska, A., *J. Inorg. Nucl. Chem.* **24**, 13 (1962).
77. Siekierska, K. E., Sokolowska, A., and Campbell, I. G., *J. Inorg. Nucl. Chem.* **12**, 18 (1959).
78. Snell, A. H., In " α , β , γ Ray Spectroscopy" (K. Siegbahn, ed.), Vol. 2, p. 1545. North-Holland Publ., Amsterdam, 1965.
79. Spano, H., and Kahn, M., *J. Amer. Chem. Soc.* **74**, 568 (1952).
80. Srinivasan, S. C., Ph.D. Thesis, Carleton Univ., Ottawa, Canada (1970).
81. Srinivasan, S. C., Wiles, D. R., and Yang, I. C., *Inorg. Nucl. Chem. Lett.*, **2**, 399 (1966).
82. Starke, K., *Naturwissenschaften* **28**, 631 (1940).
83. Starke, K., *Naturwissenschaften* **30**, 577 (1942).
84. Strohmeier, W., and Müller, R., *Z. Phys. Chem.* **40**, 85 (1964).
85. Sutin, N. and Dodson, R. W., *J. Inorg. Nucl. Chem.* **6**, 91 (1958).
86. Szilard, L. and Chalmers, T. A., *Nature (London)* **134**, 462 (1934).
87. Toropova, M. A., *J. Inorg. Chem. (USSR)* **2**, 1201 (1957).
88. Webber, I. H., Unpublished work, Carleton University, Ottawa, Canada.
89. Wexler, S., Ref. G1, Vol. I, p. 115.
90. Wheeler, O. H., and McClin, M. L., *Radiochim. Acta* **7**, 181 (1967).

91. Wheeler, O. H., and McClin, M. L., *Radiochim. Acta* **8**, 179 (1967).
92. Wheeler, O. H., Trabal, J. E., and Wiles, D. R., *Can. J. Chem.* **48**, 3609 (1970).
93. Wiles, D. R., and Wong, W. H., *Can. J. Chem.* **45**, 1813 (1967)
94. Williams, R. R., Jenks, C. H. Leslie, W. B., Richter, J. W., and Larson, Q. V., in "Radiochemical Studies: The Fission Products" (C. D. Coryell and N. Sugarman, eds.), Vol. I, p. 184. (Nat. Nucl. Energy Ser. IV, 9.) McGraw-Hill, New York, 1951.
95. Wong, W. H., and Wiles, D. R., *Can. J. Chem.* **46**, 3201 (1968).
96. Yang, I. C., and Wiles, D. R., *Can. J. Chem.* **45**, 1357 (1967).
97. Zahn, U., *Radiochim. Acta* **7**, 170 (1967).
98. Zahn, U., *Radiochim. Acta* **8**, 177 (1967).
99. Zahn, U., Collins, C. H., and Collins, K. E., *Radiochim. Acta* **11**, 33 (1969).
100. Zahn, U., and Harbottle, G., *J. Inorg. Nucl. Chem.* **28**, 925 (1966).
101. Zielinski, F. W., Ph.D. Thesis, Buffalo (1969).

Organometallic Complexes with Silicon-Transition Metal or Silicon-Carbon-Transition Metal Bonds

C. S. CUNDY, B. M. KINGSTON,¹ AND M. F. LAPPERT

*School of Molecular Sciences
University of Sussex
Brighton, England*

I. Introduction	253
II. Organometallic Complexes with Silicon-Transition Metal Bonds	254
A. Introduction and General Survey	254
B. The Synthesis of Compounds with Silicon-Transition Metal (R_3Si-M) Bonds	263
C. The Reactions of Compounds with Silicon-Transition Metal (R_3Si-M) Bonds	270
D. Structure and Bonding	280
E. Silicon-Transition Metal Complexes Having Special Structural Features.	289
III. Transition Metal-Catalyzed Homogeneous Hydrosilylation	297
A. Introduction	297
B. Chloroplatinic Acid as Catalyst	300
C. Other Transition Metal Systems as Models for the Hydrosilylation Mechanism	302
IV. Organometallic Complexes with Silicon-Carbon-Transition Metal Bonds	310
A. Introduction and General Survey	310
B. The Synthesis of Compounds with Silicon-Carbon-Transition Metal ($RR'MeSi-C-M$) Bonds	318
C. The Reactions of Compounds with Silicon-Carbon-Transition Metal ($RR'MeSi-C-M$) Bonds	321
References	323
References Added in Proof	330

I

INTRODUCTION

There is a large and growing field of transition metal chemistry in which silicon-containing ligands are involved. The object of this review is to provide a guide to the literature on those aspects of the subject described by the title and to deal in detail with topics not treated specifically elsewhere. Section II is concerned with complexes having Si-transition metal (M) bonds, Section III with the role of transition metal complexes in hydrosilylation, and Section IV with complexes having Si—C—M bonds.

¹ Present address: Careers & Appointments Advisory Service, University of Edinburgh, Edinburgh, Scotland.

TABLE I
REVIEWS RELEVANT TO SILICON-TRANSITION METAL CHEMISTRY

Subject/Title	References
σ -Complexes of Pt(II) with H, C, Si, Ge, and Sn ligands	123
Transition metal derivatives of Si, Ge, Sn, and Pb	228
Transition metal complexes with Group IVB elements	241
Silicon hydrides and their derivatives	7
Metal-metal bonds in transition metal complexes	16
Organometallic compounds with metal-metal bonds between different metals	234
Group IVB derivatives of the transition elements	40
Organic insertion reactions of Group IVB elements	180
Metal carbonyls, including silyl derivatives	1
Complexes of Pt(II) with Group IV donor ligands	243
Organometallic complexes containing Group IIIB and Group IVB ligands	115a
Chemistry of compounds containing Si-M bonds	242

Published work abstracted covers the period up to the end of 1971. References are not always given to preliminary notes and conference reports when full papers are available. A number of relevant reviews exists (see Table I).

II

ORGANOMETALLIC COMPLEXES WITH SILICON-TRANSITION METAL BONDS

A. Introduction and General Survey

Silicon-transition metal chemistry is a relatively new area. The work of Hein and his associates (1941) on Sn-Co derivatives established the possibility of forming bonds between a Group IVB metal and a transition element (139), but it was another fifteen years before $\text{CpFe(CO)}_2\text{SiMe}_3$ (203), the first of many silyl derivatives, was synthesized. The interest in these compounds derives from (1) comparison with the corresponding alkyl- and Ge-, Sn-, and Pb- transition metal (M) complexes, including the role of π -back-bonding from filled d_π orbitals of M into empty d_π orbitals on Si (or other Group IVB metal), and (2) expectation of useful catalytic properties from such heteronuclear derivatives.

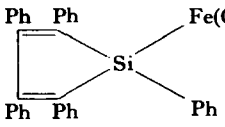
The majority of transition metal silyls (data for which are listed in Table II) contain simply one or more $-\text{SiR}_1\text{R}_2\text{R}_3$ groupings, where the groups R

TABLE II

COMPOUNDS WITH SILICON-TRANSITION METAL (R_3Si-M) BONDS

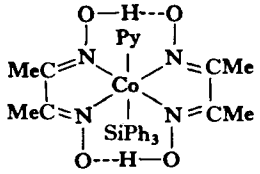
Compounds	Method of preparation ^a	References	Compounds	Method of preparation ^a	References
$(Ph_3Si)_4Ti$	2	140	$Ph_3SiMn(CO)_5$	4	94, 103, 153
$(Ph_3Si)_2TiCp_2$	2	140	$Ph_3SiMn(CO)_4PPh_3$	4, 9	103, 217
$Ph_3SiZrClCp_2$	2	48, 166	$Ph_3SiMn(CO)_3(diphos)$	9	103
$Ph_3SiHfClCp_2$	2	165, 166	$Ph_3SiMn(CO)_3(dipy)$	9	103
$H_3SiCr(CO)_3Cp$	1	124	<i>cis</i> - $Ph_3SiMnH(CO)_2(\pi-C_5H_4Me)$	8	150
$(Cl_3Si)_2Cr(CO)_2(\pi-C_6H_6)$	8/5	150	$(C_6F_5)_3SiMn(CO)_5$	4	217
<i>cis</i> - $Cl_3SiCrH(CO)_2(\pi-C_6H_6)$	8	149, 150	$(C_6F_5)_3SiMn(CO)_4PPh_3$	4, 9	217
$H_3SiMo(CO)_3Cp$	1	124	$F_3SiMn(CO)_5$	4	218
$Me_3SiMo(CO)_3Cp$	7	47, 48	$F_3SiMn(CO)_4PPh_3$	9	218
$Cl_3SiMo(CO)_3Cp$	4	148	$Cl_3SiMn(CO)_5$	4	148
$H_3SiW(CO)_3Cp$	1	124	<i>cis</i> - $Cl_3SiMnH(CO)_2Cp$	8	149, 150
$Me_3SiW(CO)_3Cp$	7	47, 48	<i>cis</i> - $Cl_3SiMnD(CO)_2Cp$	8	150
			$Cl_xH_{3-x}SiMn(CO)_5$, $x = 1-3$	10	10
			$(Cl_3Si)RMn(CO)_2Cp$, R = Cl_3Sn , Cl_2PhSn , $ClPh_2Sn$	9	152
			$(Cl_3Si)(Cl_3Sn)Mn(CO)_2(\pi-C_5H_4Me)$	9	152
			$[Cl_3SiMn(CO)_2(\pi-C_5H_4Me)]_2$	9	152
$H_3SiMn(CO)_5$	1	10	$SnCl_2$		
$D_3SiMn(CO)_5$	1	234	$[Cl_3SiMn(CO)_2Cp]^-Et_3NH^+$ or Et_4N^+	9	152
$Me_3SiMn(CO)_5$	1, 4, 5	31			
$Me_3SiMn(CO)_4PF_3$	9	31			
$Me_3SiSiMe_2Mn(CO)_5$	4	195			
$(Me_3Si)_2SiMeMn(CO)_5$	4	195			
$(Me_3Si)_3SiMn(CO)_5$	4	195			

TABLE II—continued

Compounds	Method of preparation ^a	References	Compounds	Method of preparation ^a	References
Ph ₃ SiRe(CO) ₅	4	94, 153		1	91
(C ₆ F ₅) ₃ SiRe(CO) ₅	4	217			
F ₃ SiRe(CO) ₅	4	218			
F ₃ SiRe(CO) ₄ PPh ₃	9	218			
Cl ₃ SiRe(CO) ₅	4	148			
(H ₃ Si) ₂ Fe(CO) ₄	1	12	(C ₆ F ₅) ₃ SiFe(CO) ₂ Cp	4	217
H ₃ SiFeH(CO) ₄	1	12	F ₃ SiFe(CO) ₂ Cp	10	187
(D ₃ Si) ₂ Fe(CO) ₄	1	234a	(Cl ₃ Si) ₂ Fe(CO) ₄	4	148, 150, 156
H ₃ SiFe(CO) ₂ Cp	2	4	(Cl ₃ Si) ₂ FeH(CO)Cp	4	150, 151
Me ₃ SiFe(CO) ₂ Cp	1	163, 191a, 203	(Cl ₃ Si) ₂ FeH(CO)(π -C ₅ H ₄ Me)	4	151
		163, 199	[(Cl ₃ Si) ₂ Fe(CO)Cp] ⁻ [CpFe(CO) ₃] ⁺	4	151
Me ₃ SiFe(CO)PPh ₃ Cp	9	163	[(Cl ₃ Si) ₂ Fe(CO)Cp] ⁻ [Ph ₄ As] ⁺	9	151
Me ₃ SiFe(CO)P(OPh) ₃ Cp	9	163	[(Cl ₃ Si) ₂ Fe(CO)(π -C ₅ H ₄ Me)] ⁻	4	151
Me ₃ SiFe(diphos)Cp	9	163	[(π -C ₅ H ₄ Me)Fe(CO) ₃] ⁺		
Me ₃ SiFe(Ph ₂ PCH=CHPh ₂)Cp	9	163	(Cl ₃ Si) ₂ Fe(diphos) ₂	8/5	177
Me ₃ SiFeH(CO) ₂ Cp		181	cis-Cl ₃ SiFeH(CO) ₄	8	149, 150
Me ₃ Si(SiMe ₂) _n Fe(CO) ₂ Cp,	1	164	[Cl ₃ SiFe(CO) ₄] ₂	9	150
n = 1-3			Cl ₃ SiFe(CO) ₂ Cp	1, 4	35, 148, 151, 194
(Me ₂ Si) _n [Fe(CO) ₂ Cp] ₂ , n = 2, 3	1	164	Cl ₃ SiFeH(diphos)	8	177
(Me ₂ SiC ₂ H ₄ SiMe ₂)[Fe(CO) ₂ Cp] ₂	1	164	Cl ₃ SiFeX(diphos) ₂ , X = H, Cl		177
Me ₂ HSiFe(CO) ₂ Cp	1	164	[Cl ₃ SiFe(CO) ₄] ₂ SnCl ₂	9	152
(Et ₃ Si) ₂ Fe(CO) ₄	4	156	(Cl ₃ Si)RFe(CO) ₄ , R = Cl ₃ Sn,	9	152
Ph ₃ SiFe(CO) ₂ Cp		201	Cl ₂ PhSn		
cis-Ph ₃ SiFeH(CO) ₄	8	150	[Cl ₃ SiFe(CO) ₄] ⁻ Et ₄ N ⁺ or Me ₄ N ⁺	9	152
Ph ₃ SiFe(CO) ₄ ⁻		152, 171	Cl ₂ MeSiFe(CO) ₂ Cp	4	148, 193
			Cl ₂ PhSiFe(CO) ₂ Cp	1	194
			ClPh ₂ SiFe(CO) ₂ Cp	1	194

$(\text{Me}_3\text{Si})_2\text{Ru}(\text{CO})_4$	4, 9	169	$(\text{Me}_3\text{Si})_2\text{Os}(\text{CO})_4$	4, 5	43, 170
$(\text{Me}_3\text{Si})_2\text{Ru}(\text{CO})_2(\text{PEt}_3)_2$	6	169	$\text{Me}_3\text{SiOs}(\text{CO})_4\text{X}, [\text{Me}_3\text{SiOs}(\text{CO})_4]^-$,		
$(\text{Me}_3\text{Si})_2\text{Ru}(\text{CO})_2(\text{PPh}_3)_2$	6, 8, 9	169	$\text{X} = \text{H}, \text{D}$	4	170
$\text{Me}_3\text{SiRu}(\text{CO})_4\text{X}, [\text{Me}_3\text{SiRu}(\text{CO})_4]^-$,			$\text{X} = \text{H}, \text{Me}, \text{SnMe}_3$,	9	170
$\text{X} = \text{Me}_3\text{Sn}, \text{Ph}_3\text{Sn}, \text{Ph}_3\text{PAu},$	9	169	$\text{Ru}(\text{CO})_4\text{SiMe}_3, \text{CF}_2\text{CF}_2\text{H}$		
$\text{Mn}(\text{CO})_5, \text{Bu}_3\text{Ge}$			$\text{X} = \text{AuPPh}_3$	9	168
$\text{X} = \text{I}, \text{Br}, \text{Re}(\text{CO})_5$	9	6	$\text{X} = \text{Br}, \text{I}$	9	6
$\text{X} = \text{Os}(\text{CO})_4\text{SiMe}_3$	9	170	$\text{Me}_3\text{SiOsMe}(\text{CO})_3\text{PPh}_3$	9	170
$\text{Me}_3\text{SiRu}(\text{CO})_3(\text{PPh}_3)\text{X}, \text{X} = \text{I}, \text{H}$	9	6	$\text{Me}_3\text{SiOsX}(\text{CO})_3\text{PPh}_3, \text{X} = \text{Br}, \text{I}$	9	6
$[\text{Me}_3\text{SiRu}(\text{CO})_4]_2$	4	169	$[\text{Me}_3\text{SiOs}(\text{CO})_4]_2$	4, 9	170
$[\text{Me}_3\text{SiRu}(\text{CO})_3\text{X}]_2, \text{X} = \text{Br}, \text{I}$	9	6	$[\text{Me}_3\text{SiOs}(\text{CO})_3\text{X}]_2, \text{X} = \text{Br}, \text{I}$	9	6
$[\text{Et}_3\text{SiRu}(\text{CO})_4]_2$	4	169	$(\text{Et}_3\text{Si})_2\text{Os}(\text{CO})_4$	4	170
$\text{Et}_3\text{SiRu}(\text{CO})_4\text{SnMe}_3$	9	169	$\text{Et}_3\text{SiOs}(\text{CO})_4\text{H}$	4	170
$[\text{Pr}_3\text{SiRu}(\text{CO})_4]_2$	4	169	$[\text{Et}_3\text{SiOs}(\text{CO})_4]_2$	4	170
$[\text{Ph}_3\text{SiRu}(\text{CO})_4]_2$	4	169			
$[(\text{EtO})_3\text{SiRu}(\text{CO})_4]_2$	4	169	$\text{H}_3\text{SiCo}(\text{CO})_4$	1	9
$(\text{Cl}_3\text{Si})_2\text{Ru}(\text{CO})_4$	4	169	$\text{H}_3\text{SiCo}(\text{CO})_3\text{PPh}_3$	9	9
$(\text{Cl}_3\text{Si})_2\text{Ru}(\text{CO})_2(\text{PPh}_3)_2$	9	169	$\text{D}_3\text{SiCo}(\text{CO})_4$	1	234a
$[\text{Cl}_3\text{SiRu}(\text{CO})_4]_2$	4	169	$\text{H}_2\text{Si}[\text{Co}(\text{CO})_4]_2$	1	9
$\text{Cl}_3\text{SiRu}(\text{CO})_4\text{Br}$	9	6	$\text{H}_2\text{MeSiCo}(\text{CO})_4$	4, 5	13, 117, 125
$\text{Cl}_3\text{SiRu}(\text{CO})_2\text{Cp}$	4	35	$\text{HPh}_2\text{SiCo}(\text{CO})_4$	4	57
$[\text{Cl}_2\text{MeSiRu}(\text{CO})_4]_2$	4	169	$\text{Me}_3\text{SiCo}(\text{CO})_4$	4, 5	13, 14, 125, 189
			$[\text{MeSi}(\text{O})\text{Co}(\text{CO})_4]_4$	4	56, 57
			$\text{Et}_3\text{SiCo}(\text{CO})_4$	4	56, 57, 95, 155, 156, 223
			$\text{Et}_3\text{SiCo}(\text{CO})_3\text{PEt}_3$	9	156
			$\text{Et}_3\text{SiCo}(\text{CO})_3\text{PPh}_3$		182
			$\text{Ph}_3\text{SiCo}(\text{CO})_4$	4, 5	56, 57, 95, 155, 156, 223

TABLE II—continued

Compounds	Method of preparation ^a	References	Compounds	Method of preparation ^a	References
$\text{Ph}_3\text{SiCo}(\text{CO})_3\text{PPh}_3$	1	92	$\text{HPPh}_2\text{SiRhH}(\text{Cl})(\text{PPh}_3)_2$	8	60
	6	216a	$\text{Me}_3\text{SiRhH}(\text{Cl})(\text{PPh}_3)_2$	8	60, 135
$\text{PhMeRSiCo}(\text{CO})_4$, R = α -naphthyl, neopentyl	4	223	$\text{Me}_3\text{SiRhH}(\text{CO})\text{Cl}(\text{PEt}_3)_2$	8	60
$(\text{C}_6\text{F}_5)_3\text{SiCo}(\text{CO})_4$	4	217	$\text{Me}(\text{OSiMe}_3)_2\text{SiRhH}(\text{Cl})(\text{PPh}_3)_2$	8	113
$(\text{MeO})_3\text{SiCo}(\text{CO})_4$	4	56, 155, 156	$\text{Et}_3\text{SiRhH}(\text{X})(\text{PPh}_3)_2$, X = Cl, Br	8	135
$(\text{EtO})_3\text{SiCo}(\text{CO})_4$	4	57	$\text{Ph}_3\text{SiRhH}(\text{Cl})(\text{PPh}_3)_2$	8	135
$(\text{EtO})_3\text{SiCoH}_2(\text{PPh}_3)_2$	8	5	$(\text{EtO})_3\text{SiRhH}(\text{X})(\text{PPh}_3)_2$, X = Cl, Br, I	8	135
$\text{F}_3\text{SiCo}(\text{CO})_4$	4, 10	125, 126, 187, 189, 210	$(\text{EtO})_3\text{SiRhH}(\text{Cl})(\text{AsPh}_3)_2$	8	135
$\text{F}_3\text{SiCoH}_2(\text{PPh}_3)_2$	8	5	$(\text{EtO})_3\text{SiRhH}(\text{Cl})(\text{SbPh}_3)_2$	8	135
$\text{F}_2\text{MeSiCo}(\text{CO})_4$	4, 5	116, 117	$(\text{Cl}_3\text{Si})_3\text{Rh}(\text{PPh}_3)_2$	5/8	113
$(\text{Cl}_3\text{Si})_2\text{Co}(\text{CO})\text{Cp}$		121, 175	$(\text{Cl}_3\text{Si})_2\text{RhCl}(\text{PPh}_3)_2$	5	135
$\text{Cl}_3\text{SiCo}(\text{CO})_4$	4, 5	13, 14, 56, 57	$(\text{Cl}_3\text{Si})_2\text{RhCl}(\text{cyclooctadiene})$	8/5	113
		95, 125, 155, 156, 189, 206	$(\text{Cl}_3\text{Si})_2\text{Rh}(\text{C}_2\text{H}_4)\text{Cp}$	8/5	113
$\text{Cl}_3\text{SiCo}(\text{CO})_3\text{PEt}_3$	9	156	$(\text{Cl}_3\text{Si})_2\text{Rh}(\text{cyclooctene})\text{Cp}$	8	113
$\text{Cl}_3\text{SiCo}(\text{CO})_3\text{PF}_3$		182	$\text{Cl}_3\text{SiRh}(\text{X})(\text{PPh}_3)_2$, X = Cl	8	60, 135
$\text{Cl}_3\text{SiCo}(\text{CO})_3\text{PBU}_3$	9	196a	X = Br, I	8	135
$\text{Cl}_3\text{SiCoH}(\text{CO})\text{Cp}$	8	149, 150	$\text{Cl}_3\text{SiRhH}(\text{Cl})(\text{AsPh}_3)_2$	8	135
$\text{Cl}_2\text{PhSiCo}(\text{CO})_4$	4	56, 57, 125	$\text{Cl}_3\text{SiRhH}(\text{Cl})(\text{SbPh}_3)_2$	8	135
			$\text{Cl}_3\text{SiRhH}(\text{CO})\text{Cl}(\text{PPh}_3)_2$	8	60, 135
			$\text{Cl}_3\text{SiRhH}(\text{CO})\text{Cl}(\text{PEt}_3)_2$	8	60
			$\text{Cl}_3\text{SiRhH}(\text{CO})\text{Cl}(\text{solvent})_2$		60
			$\text{Cl}_2\text{MeSiRhH}(\text{Cl})(\text{PPh}_3)_2$	8	60, 135
			$\text{Cl}_2\text{MeSiRhH}(\text{Br})(\text{PPh}_3)_2$	8	135
			$\text{Cl}_2\text{MeSiRhH}(\text{CO})\text{Cl}(\text{PEt}_3)_2$	8	60
			$\text{Cl}_2\text{EtSiRhH}(\text{X})(\text{PPh}_3)_2$, X = Cl, Br	8	135
			$\text{ClMe}_2\text{SiRhH}(\text{X})(\text{PPh}_3)_2$, X = Cl, Br	8	135
			$\text{ClEt}_2\text{SiRhH}(\text{X})(\text{PPh}_3)_2$, X = Cl, Br	8	135
			$(\text{PhCH}_2)_3\text{SiRhH}(\text{CO})\text{Cp}$	8	196b
			$\text{Ph}_3\text{SiRhH}(\text{CO})\text{Cp}$	8	196b
			$\text{Ph}_3\text{SiRh}(\text{PF}_3)_4$	4, 5	25b

(EtO) ₃ SiRh(PF ₃) ₄	4, 5	25b		
(Cl ₃ Si) ₂ Rh(CO)Cp	8/5	196b		
Cl ₃ SiRh(PF ₃) ₄	4, 5	25b		
(Cl ₂ MeSi) ₂ Rh(CO)Cp	8/5	196b		
(Me ₃ Si) ₂ Ir(HgSiMe ₃)CO(PET ₃) ₂	3/8	141		
Et ₃ SiIrH ₂ (CO)(PPh ₃) ₂	8	51		
Ph ₃ SiIrH ₂ (CO)(PPh ₃) ₂	8	131		
Ph ₃ SiIr(PF ₃) ₄	4, 5	25b		
(EtO) ₃ SiIrH(CO)Cl(PPh ₃) ₂	8	55		
(EtO) ₃ SiIrH ₂ (CO)(PPh ₃) ₂	8	51, 131		
[(EtO) ₃ SiIrH(diphos) ₂] ⁺ [BPh ₄] ⁻	8	133		
Cl ₃ SiIrH(CO)Cl(PPh ₃) ₂	8	55		
Cl ₃ SiIrH ₂ (CO)(PPh ₃) ₂	8	131		
Cl ₂ EtSiIrH(CO)Cl(PPh ₃) ₂	8	55		
Cl ₂ PhSiIrH(CO)Cl(PPh ₃) ₂	8	55		
[Ph ₃ SiNi(CO) ₃] ⁻ Li ⁺ · 2THF		171		
[Ph ₃ SiNi(CO) ₃] ⁻ Me ₄ N ⁺		171		
(Cl ₃ Si) ₂ Ni(dipy)		167		
Cl ₃ SiNi(CO)Cp	4	148		
Cl ₃ SiNi(PPh ₃)Cp	6	216		
(Cl ₂ MeSi) ₂ Ni(dipy)		167		
<i>trans</i> -H ₃ SiPtX(PET ₃) ₂ , X = Cl, Br, I	5	27		
<i>trans</i> -H ₂ FSiPtCl(PET ₃) ₂	5	27		
<i>trans</i> -H ₂ ClSiPtX(PET ₃) ₂ , X = Cl, Br, I	5	27		
H ₂ ClSiPtI ₂ (H)(PET ₃) ₂	8	27		
<i>trans</i> -H ₂ BrSiPtX(PET ₃) ₂ , X = Br, I	5	27		
<i>trans</i> -H ₂ ISiPtI(PET ₃) ₂	5	27		
H ₂ ISiPtI ₂ (H)(PET ₃) ₂	8	27		
<i>trans</i> -H ₂ (NMe ₂) ₂ SiPtCl(PET ₃) ₂	5	27		
<i>trans</i> -HCl ₂ SiPtX(PET ₃) ₂ , X = Cl, I	5	27		
<i>trans</i> -HI ₂ SiPtI(PET ₃) ₂	5	27		
(HPh ₂ Si) ₂ Pt(diphos)	8	65		
(Me ₃ Si) ₂ Pt(diphos)	3	71		
Me ₃ SiPtCl(diphos)	3	69, 71		
<i>trans</i> -Me ₃ SiPtCl(PET ₃) ₂	3	114		
<i>trans</i> -Me ₃ SiPt(GePh ₃)(PET ₃) ₂	9	114		
[Me ₃ SiPt(PET ₃) ₂ diphos] ⁺ X ⁻ , X = Cl, BPh ₄	9	115		
<i>cis</i> -(Me ₂ PhSi) ₂ Pt(PMePh) ₂	2	63		
<i>cis</i> -(MePh ₂ Si) ₂ Pt(PMe ₂ Ph) ₂	2	63		
(MePh ₂ Si) ₂ Pt(diphos)	2, 9	63, 65		
<i>trans</i> -(MePh ₂ Si)PtCl(QMe ₂ Ph) ₂ , Q = P, As	6	63		
(+)- <i>trans</i> -PhMe(α-Np)SiPtCl(PMe ₂ Ph) ₂	6	105a		
Ph ₃ SiPt(H)(PET ₃) ₂	2	15		
<i>trans</i> -Ph ₃ SiPtCl(PMe ₂ Ph) ₂	5	63		
<i>trans</i> -Ph ₃ SiPtBr(PMe ₂ Ph) ₂	6	63		
<i>trans</i> -Ph ₃ SiPtCl(AsMe ₂ Ph) ₂	6	63		
<i>trans</i> -Ph ₃ SiPtX(PMe ₂ Ph) ₂ , X = I, SCN, N ₃ , SnCl ₃ , SnBr ₃ , InCl ₂ , C ₆ H ₅ , <i>m</i> - or <i>p</i> -C ₆ H ₄ F	9	64		
<i>cis</i> -Ph ₃ SiPt(C ₆ F ₅)(PMe ₂ Ph) ₂	9	64		
<i>trans</i> -Ph ₃ SiPtX(AsMe ₂ Ph) ₂ , X = Br, I, SCN, N ₃	9	64		
<i>trans</i> -R ₃ SiPtCl(PMe ₂ Ph) ₂ , R = C ₆ F ₅ , <i>m</i> -FC ₆ H ₄ , <i>p</i> -ClC ₆ H ₄ , <i>m</i> -CF ₃ C ₆ H ₄ , <i>p</i> -CF ₃ C ₆ H ₄ , <i>p</i> -MeC ₆ H ₄ , <i>p</i> -MeOC ₆ H ₄ , <i>p</i> -Me ₂ NC ₆ H ₄	5	63		
<i>trans</i> -R ₃ SiPtBr(PMe ₂ Ph) ₂ , R = <i>p</i> -ClC ₆ H ₄ , <i>m</i> -CF ₃ C ₆ H ₄ , <i>p</i> -MeC ₆ H ₄	5	63		

TABLE II—continued

Compounds	Method of preparation ^a	References	Compounds	Method of preparation ^a	References
<i>trans</i> -R ₃ SiPtCl(PMe ₂ Ph) ₂ , R = <i>m</i> -ClC ₆ H ₄ , <i>m</i> -MeC ₆ H ₄	6	63	(Ph ₂ BrSi) ₂ Pt(diphos)	7	65
<i>trans</i> -R ₃ SiPtBr(PMe ₂ Ph) ₂ , R = <i>p</i> -Me ₂ NC ₆ H ₄	6	63	<i>cis</i> -(Cl ₃ Si) ₂ Pt(PPh ₃) ₂	8	65, 215
<i>trans</i> -R ₃ SiPtCl(AsMe ₂ Ph) ₂ , R = <i>m</i> -FC ₆ H ₄ , <i>m</i> -ClC ₆ H ₄ , <i>p</i> -ClC ₆ H ₄ , <i>m</i> -MeC ₆ H ₄ , <i>p</i> -MeC ₆ H ₄ , <i>m</i> -CF ₃ C ₆ H ₄ , <i>p</i> -CF ₃ C ₆ H ₄ , <i>p</i> -Me ₂ NC ₆ H ₄ , <i>p</i> -MeOC ₆ H ₄	6	63	(Cl ₃ Si) ₂ Pt(diphos)	8	65
			(Cl ₃ Si)PtH(diphos)	8	65
			<i>trans</i> -(Cl ₃ Si)PtCl(PEt ₃) ₂	5	27
			(Cl ₃ SiPtPCl ₃) _x	6	237
			<i>cis</i> -(Cl ₂ MeSi) ₂ Pt(PPh ₃) ₂	8	90, 110a, 240
			<i>cis</i> -Cl ₂ MeSiPtH(PPh ₃) ₂	5	90, 110a, 240
<i>cis</i> -R ₃ SiPtH(PPh ₃) ₂ , R = <i>m</i> -FC ₆ H ₄ , <i>p</i> -FC ₆ H ₄ , <i>m</i> -CF ₃ C ₆ H ₄ , <i>p</i> -CF ₃ -C ₆ H ₄	8	65	[Ph ₃ SiCu]		111
			Ph ₃ SiAuPPh ₃		15

^a Numbers refer to 1, reaction of a transition metal anion with a silicon halide; 2, reaction of an alkali metal silyl with a transition metal halide; 3, the mercurial route; 4, reaction of an SiH compound involving cleavage of a metal-metal bond; 5, reaction of an SiH compound with a transition metal hydride involving elimination of H₂; 6, elimination of a hydrogen halide; 7, elimination of an amine; 8, oxidative addition or elimination; 9, from an SiM precursor, involving substitution at M; 10, from an SiM precursor, involving substitution at Si; 11, from an Si₂M precursor, involving cleavage of one SiM bond.

Diphos = Ph₂PCH₂CH₂PPh₂.

are usually alkyl, aryl, hydrogen, halogen, alkoxy, silyl, or polysilyl. There exists, however, a smaller family of more complex compounds, listed in Table III, which are discussed in Section II,E. Unsubstantiated patent reports (118), covering derivatives of Ti, Zr, V, Nb, Ta, W, Mn, Re, and Ni are excluded, and a report of titanium complexes (140) has been questioned (166).

The distribution of silyls among the transition elements is rather similar to that of the alkyls; complexes are generally diamagnetic and formal oxidation states of +4 (Ti, Zr, Hf, Fe, Pt), +3 (Mn, Co, Rh, Ir), +2 (Cr, Mo, W, Fe, Ru, Os, Ni, Pt), +1 (Mn, Re, Co, Cu, Au), and 0 (Fe, Ru, Os, Ni) are represented. Derivatives of Group V metals, Ag and Tc are still unknown, and of Groups IVA and IB are rare. Derivatives of Group VI, Mn, Re, the iron group, and Co are mostly carbonyls or cyclopentadienyl carbonyls. The growing number of compounds of Rh, Ir, and Pt reflects the current interest in the platinum metals in general and the utilization in synthesis of oxidative addition (or elimination). Silyls and alkyls of Ni, especially those not containing the stabilizing CpNi(L) unit, are still a rarity, and no well-characterized [but see Section II,B,5] Pd derivative has yet been reported. A more extensive silicon chemistry of Ni, Pd, and the early transition metals

TABLE III

SILICON-TRANSITION METAL COMPLEXES WITH SPECIAL STRUCTURAL FEATURES

Compounds	Comments	References
$(\text{Et}_2\text{Si})_2\text{H}_2\text{W}_2(\text{CO})_8$	2Si—H—W bridges	26, 26a
$(\text{Ph}_2\text{Si})_2[\text{Mn}(\text{CO})_4]_2$	Si—Mn—Si—Mn metallo-cycle	142
$\text{Ph}_3\text{SiHMn}(\text{CO})_2\text{Cp}$	Si—H—Mn bridge located (X-ray)	26, 120
$\text{Me}_3\text{SiH}_2\text{Re}_2(\text{CO})_8$	} 2 Si—H—Re bridges	108, 143
$\text{Ph}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$		143
$\text{Ph}_2\text{SiD}_2\text{Re}_2(\text{CO})_8$	} 4 Si—H—Re bridges	143
$(\text{Et}_2\text{SiH}_2)_2\text{Re}_2(\text{CO})_6$		26
$[\text{Me}_3\text{SiHFe}(\text{CO})_4]_2$	} See Section II,E,6	192, 192a
$[(\text{Me}_3\text{Si})_2\text{Fe}(\text{CO})_4]_2$		192, 192a
$(\text{Me}_3\text{Si})_2\text{Fe}_2(\text{CO})_7$	2 (Me ₂ Si) bridges and 1 CO bridge	174

TABLE III—*continued*

Compounds	Comments	References
$[\text{R}_2\text{Si}(\text{CH}_2)_3]\text{Fe}(\text{CO})_4$, $\text{R}_2 = \text{Me}_2, (\text{OMe})_2, \text{MeCl}$ $[\text{Me}_2\text{Si}\{\text{CH}_2(\text{SiMe}_2)\text{CH}_2\}]\text{Fe}(\text{CO})_4$ $[\text{Me}_2\text{Si}(\text{CH}_2\text{C}_6\text{H}_4)]\text{Fe}(\text{CO})_4$	$\left. \begin{array}{l} \\ \\ \\ \end{array} \right\}$ Metallocycle derivatives of silacyclobutanes	89, 90
$\text{Ph}_2\text{SiFe}_2(\text{CO})_3\text{Cp}_2$		68
$[\text{Cl}_2\text{SiFe}(\text{CO})_4]_2$	Si—Fe—Si—Fe metallocycle	96, 148
$\text{Me}_3\text{SiRu}(\text{CO})_3(\text{SiMe}_2)_2(\text{CO})_3\text{RuSiMe}_3$	2 (Me_2Si) bridges	39
$(\text{CO})_3\text{Ru}(\text{SiMe}_2)_3\text{Ru}(\text{CO})_3$	3 (Me_2Si) bridges	39
$\text{Me}_3\text{SiOs}(\text{CO})_3(\text{SiMe}_2)_2(\text{CO})_3\text{OsSiMe}_3$	2 (Me_2Si) bridges	39
$[\text{Me}_2\text{SiOs}(\text{CO})_3]_3$	3 (Me_2Si) bridges	39
$(\text{CH}_2=\text{CH})\text{SiCo}_3(\text{CO})_9$	$\left. \begin{array}{l} \\ \end{array} \right\}$ Clusters with Co—Co bonds (?)	161
$[\text{SiCo}_3(\text{CO})_9]_2$		162
$\text{Ph}_2\text{SiCo}_2(\text{CO})_7$	1 (Ph_2Si) bridge and 1 CO bridge	18
$\text{PhSi}[\text{Co}_3(\text{CO})_{11}]$	1 $[(\text{CO})_4\text{Co}]\text{PhSi}$ bridge and 1 CO bridge	18
$\text{R}_3\text{SiCo}_3(\text{CO})_{10}$, $\text{R} = \text{Me}, \text{Ph}$	$\text{R}_3\text{Si—O—}$ bonded to $\text{CCo}_3(\text{CO})_9$ cluster	183
$\text{R}_2\text{SiCo}_4(\text{CO})_{14}$, $\text{R} = \text{Et}, \text{Ph}$	$(\text{CO})_4\text{CoSi—O—}$ bonded to $\text{CCo}_3(\text{CO})_9$ cluster	110
$[(\text{diphos})_2\text{CoH}_2]^+[\text{SiXYZ}]^-$ $\text{XYZ} = \text{Cl}_3\text{Cl}_2\text{Me}, \text{ClMe}_2, \text{ClPh}_2$	Silyl group present as anion (?)	177
$[\text{Cl}_2\text{SiNi}(\text{PPh}_3)_2]\text{x}$	Si—Ni—Si—Ni metallocycle ($\text{x} = 2$)(?)	177
$[(\text{diphos})_2\text{NiX}]^+[\text{SiCl}_3]^-$ $\text{X} = \text{H}$ or SiCl_3	Silyl group present as anion(?)	177
$(\text{X}_2\text{Si})_2\text{Pt}(\text{PPh}_3)_2$, $\text{X} = \text{Cl}$ or Br	Silylene ligands(?)	215
$(\text{Cl}_2\text{MeSi})_2\text{Pt}_2(\text{PPh}_3)_4$	Mixed valence dimer with bridging (SiMeCl_2) groups	110a

will undoubtedly develop as the problems of ancillary ligand selection and experimental technique in these reactive systems are overcome. In general, electronegative substituents at Si give greater stability (e.g., decreasing stability in the order $\text{Cl}_3\text{Si} > \text{Ar}_3\text{Si} > \text{R}_3\text{Si}$), a situation parallel to that found for alkyls. Unsubstituted silyl compounds ($\text{H}_3\text{Si—M}$) are less stable than higher homologs (e.g., $\text{Me}_3\text{Si—M}$). This contrasts with the alkyls ($\text{H}_3\text{C—M}$ usually more stable than $\text{C}_2\text{H}_5\text{—M}$), for which an olefin-elimination pathway in higher homologs provides a common decomposition

route; this is not available for silicon analogs; sila-olefins, >Si=C< , are unknown.

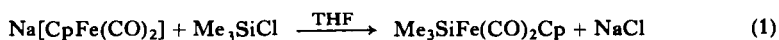
Nearly all the presently known compounds contain one or more π -acceptor ligands (e.g., CO, Cp, R_3P) on the transition metal. These ligands may, as has classically been assumed for alkyls (72), dissipate some of the negative charge density on the central metal. However, it will be stressed later (Section IV) that such stabilizing ligands are unnecessary, and their role may in any case be more complex.

B. The Synthesis of Compounds with Silicon-Transition Metal ($\text{R}_3\text{Si-M}$) Bonds

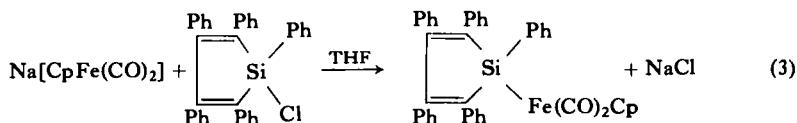
The major synthetic routes to transition metal silyls fall into four main classes: (1) salt elimination, (2) the mercurial route, a modification of (1), (3) elimination of a covalent molecule (H_2 , HHal , or R_2NH), and (4) oxidative addition or elimination. Additionally, (5) there are syntheses from Si—M precursors. Reactions (1), (2), and (4), but not (3), have precedence in C—M chemistry. Insertion reactions of Si(II) species (silylenes) have not yet been used to form Si—M bonds, although work may be stimulated by recent reports of $\text{Me}_2\text{Si:}$ (147) and $\text{F}_2\text{Si:}$ (185). A new development has been the use of a strained silicon heterocycle as starting material (Section II,E,4).

1. Salt Elimination: Reaction of a Transition Metal Anion with a Silicon Halide

Salt elimination was used by Piper, Lemal, and Wilkinson (203) to obtain the first compound containing an Si—M bond [Eq. (1)]. The same procedure



afforded a series of stable polysilyl derivatives (164) [Eq. (2) ($n = 1, 2, 3$)] and cyclic silicon compounds: [Eq. (3)] (91) and $\text{CpFe}(\text{CO})_2\text{Si}(\text{Me})\text{CH}_2\text{CH}_2\text{CH}_2$ (90).



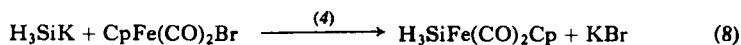
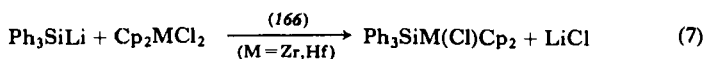
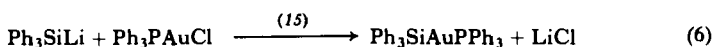
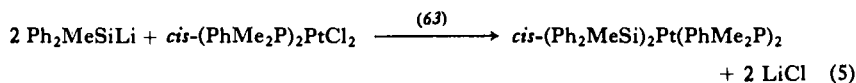
$\text{Ph}_3\text{SiCo}(\text{CO})_3\text{PPh}_3$ was similarly obtained from $\text{Na}[\text{Co}(\text{CO})_3\text{PPh}_3]$ (92). However, such reactions have often failed to yield an $\text{Si}-\text{M}$ complex, and disiloxanes were isolated (92, 92a). It was concluded that the oxygen derived from the carbonyl groups of the anions, and that the primary reaction involves nucleophilic attack by the carbonyl oxygen. This view is supported by the isolation of compounds containing $\text{Si}-\text{O}-\text{C}-\text{M}$ linkages from reactions of $\text{Na}_2\text{Fe}(\text{CO})_4$ (in THF) (192) and $\text{Li}[\text{Co}_3(\text{CO})_{10}]$ (in diethyl ether) (183) (see Section II,E,6).

$\text{H}_3\text{SiCo}(\text{CO})_4$, $\text{H}_2\text{Si}[\text{Co}(\text{CO})_4]_2$, and $\text{H}_3\text{SiMn}(\text{CO})_5$ were prepared from the appropriate carbonyl anion and halosilane in the presence of an ether (10), whereas $\text{Na}_2\text{Fe}(\text{CO})_4$ and H_3SiI , after removal of THF, gave $(\text{H}_3\text{Si})_2\text{Fe}(\text{CO})_4$ and $\text{H}_3\text{Si}(\text{H})\text{Fe}(\text{CO})_4$ (12). $\text{Me}_3\text{SiMn}(\text{CO})_5$ (36%) was obtained from liquid Me_3SiCl and solid $\text{NaMn}(\text{CO})_5$ in the absence of solvent (31); reactions according to Eq. (4) ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) (20–40%) were also conducted in the absence of solvents (124).



2. Salt Elimination: Reaction of an Alkali Metal Silyl with a Transition Metal Halide

Equations (5)–(8) illustrate the use of this reverse salt elimination procedure.

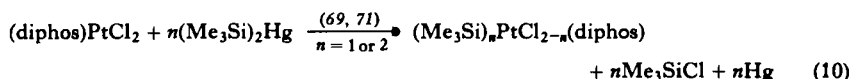


Limitations common to both salt elimination methods 1 and 2 are (a) the required product may be difficult to separate from the alkali metal halide, (b) reactions are best carried out in the solvent (usually an ether) in which the initial alkali metal derivative is prepared, (c) difficulties may arise through metal-halogen exchange (201), and (d) the range of starting anions is limited [e.g., X_3Si^- compounds are only readily formed when $\text{X} = \text{H}$ or Ar ,

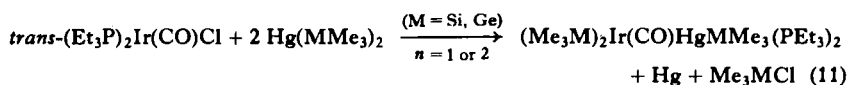
and suitable transition metal anions are $\text{CpM}(\text{CO})_n^-$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$, with $n = 3$; $\text{M} = \text{Fe}$, with $n = 2$), $\text{Mn}(\text{CO})_5^-$, $\text{Re}(\text{CO})_5^-$, $\text{Co}(\text{CO})_4^-$, and $\text{Fe}(\text{CO})_4^{2-}$].

3. The Mercurial Route

A particular case of the limitation (d) of the preceding paragraph arises since the peralkyl derivatives of alkali metals are not readily accessible (112, 214). This problem has been overcome in some cases [Eqs. (9), (10); $n = 1$ or 2] by the use of a mercurial silylating agent, but the method has not

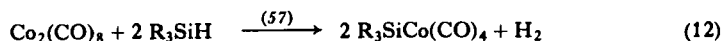


been widely used. The failure to introduce two trimethylsilyl groups in this way when the nonchelating Et_3P was used was ascribed to the high trans effect of the silyl ligand (61, 71). A more complex reaction, involving both halogen replacement and oxidative addition, is shown in Eq. (11) (141).



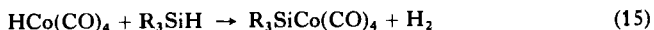
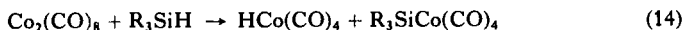
4. Hydrogen Elimination

Two closely related reactions, (a) and (b), illustrated by Eq. (12) ($\text{R}_3 = \text{HPh}_2, \text{Et}_3, \text{Ph}_3, \text{Cl}_3, \text{Cl}_2\text{Ph}$) and (13), of silicon hydrides with transition metal complexes generate compounds with Si—M bonds with elimination of hydrogen: (a) cleavage of metal—metal bonds and (b) reaction with transition metal hydrides. Reactions discussed in this section are relevant to



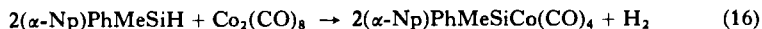
hydrosilylation (Section III). The reaction sequence proposed for Eq. (12)

is shown in Eqs. (14) and (15); by using the stoichiometry of Eq. (14), $\text{HCo}(\text{CO})_4$ was isolated (57).



$\text{Me}_3\text{SiMn}(\text{CO})_5$ has also been obtained from $\text{Mn}_2(\text{CO})_{10}$, and $\text{HMn}(\text{CO})_5$ was a postulated intermediate (31). Thus, method (a) comprises a formally oxidative M—M cleavage and a subsequent hydrogen elimination between Si—H and H—M moieties.

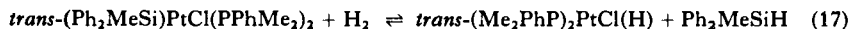
The synthesis of the first optically active compound is illustrated in Eq. (16); it was obtained with retention (>85%) of configuration about silicon (223).



The reaction of $[\text{CpFe}(\text{CO})_2]_2$ with Cl_3SiH gave four complexes $\{\text{Cl}_3\text{SiFe}(\text{CO})_2\text{Cp}$, $(\text{Cl}_3\text{Si})_2\text{FeH}(\text{CO})\text{Cp}$, $[\text{CpFe}(\text{CO})_3]^+[(\text{Cl}_3\text{Si})_2\text{Fe}(\text{CO})\text{Cp}]^-$, and $[\text{CpFe}(\text{CO})_3]^+\text{FeCl}_4^-\}$ (151). $(\text{Cl}_3\text{Si})_2\text{FeH}(\text{CO})\text{Cp}$ is remarkable in being highly dissociated in MeCN, and is second only to HClO_4 in acid strength in MeCN; addition of $[\text{Ph}_4\text{As}]^+\text{Cl}^-$ gives $[\text{Ph}_4\text{As}]^+[(\text{Cl}_3\text{Si})_2\text{Fe}(\text{CO})\text{Cp}]^-$.

Reactions of R_3SiH and $\text{M}_3(\text{CO})_{12}$ ($\text{M} = \text{Fe}$, Ru , Os) gave various complexes: $(\text{R}_3\text{Si})_2\text{M}(\text{CO})_4$ [$\text{M} = \text{Fe}$ (156), Ru (169), Os (170)]; and $\text{R}_3\text{SiM}(\text{CO})_4-(\text{CO})_4\text{MSiR}_3$ [$\text{M} = \text{Ru}$ (169), Os (170)]. Hydrides, e.g., $\text{R}_3\text{SiOs}(\text{CO})_4\text{H}$, were also isolated and these were regarded as the probable initial products (170).

The discovery of the reversibility of the system of Eq. (17) (62) has led to a useful synthesis of Si—Pt complexes (63).



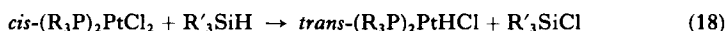
The ease of such reactions is dependent on ligands attached to Pt and Si. Thus, $\text{trans}-(\text{Me}_2\text{PhP})_2\text{PtHCl}$ gave complexes with a number of triaryl-silanes, whereas $\text{trans}-(\text{Et}_3\text{P})_2\text{PtHCl}$ did not react with Ph_3SiH , and $\text{trans}-(\text{Ph}_3\text{P})_2\text{PtHCl}$ underwent only slow chlorination with Cl_3SiH (63). However, $\text{trans}-(\text{Et}_3\text{P})_2\text{PtHX}$ reacted readily with (among others) the compounds H_3SiX ($\text{X} = \text{Cl}$, Br , I) to form $\text{trans-H}_2\text{XSiPtX}(\text{PEt}_3)_2$ (27).

Hydrogenation of silylplatinum(II) complexes is further discussed in Section II,C,3,c.

An obvious limitation to the hydrogen-elimination method, especially for early transition metal elements, is the availability of transition metal hydrides (this applies also to the HCl elimination) or binuclear complexes.

5. Hydrogen Halide Elimination

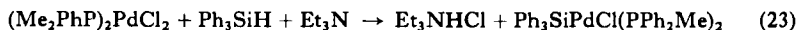
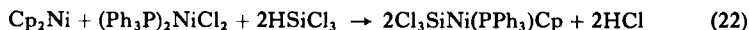
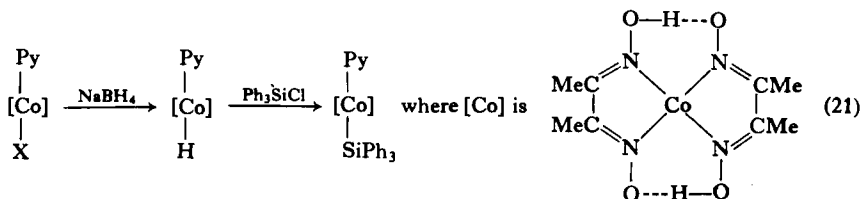
Reactions of silicon hydrides with *cis*-(R₃P)₂PtCl₂ (R = Bu, Ph) have been widely investigated. Alkyl- and aryl-silanes underwent metathetical H/Cl exchange [Eq. (18) (R' = Et, Ph, PhCH₂, C₆H₁₃)] (55).



Silanes with electronegative ligands did not react, except in the presence of the tertiary base Et₃N [e.g., Eq. (19)] (62, 63). This then provides an attractive route to Si—Pt(II) compounds since the starting materials are readily available and the reaction gives pure products in high (60–90%) yields. Only aromatic phosphine Pt complexes reacted readily, and the use of an excess of silane failed to bring about replacement of the second halogen atom.



A Ru—Si complex (169), a cobaloxime derivative (216a), a Ni complex (216), and the reported Pd compound (obtained in an impure state) (158) have also been made [Eqs. (20)–(23)].



6. Amine Elimination

This method was used to prepare Group VI complexes, as shown in Eq. (24) (M = Cr; M' = Ge, Sn. M = Mo, W; M' = Si, Ge, Sn) (47); reactivity decreases in the series CrH > MoH > WH and SnN > GeN ~ SiN.

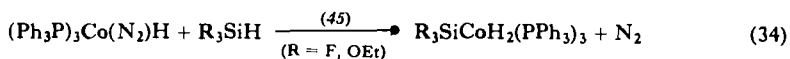
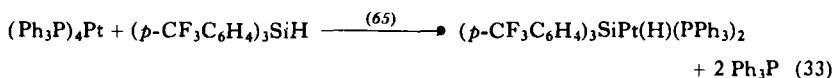
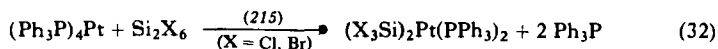
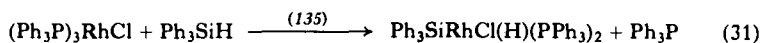
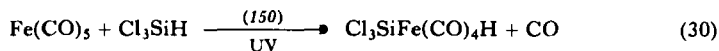
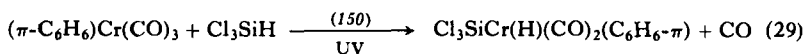
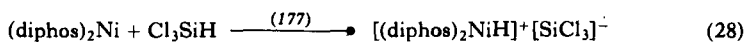
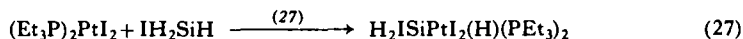
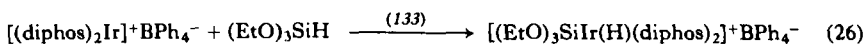
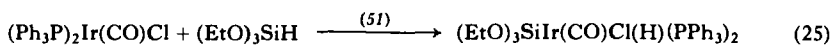
Reaction of $\text{Me}_3\text{SiNMe}_2$ with HCo(L)_4 gave $[\text{Me}_3\text{SiNHMe}_2]^+[\text{Co(L)}_4]^-$, $\text{L} = \text{CO}$ or PF_3 (140a).



The reaction offers similar advantages to those of molecular hydrogen elimination, but is complementary (i.e., amine elimination is suitable for Group VI but not Pt, and conversely for H_2 elimination) in that conditions are mild, yields high, and the volatile by-product easily removed. Previous attempts to prepare Group VIA silicon compounds by a salt elimination procedure proved unsuccessful (201). However, compounds having metal-metal bonds between elements of Groups IVA and IVB could only be synthesized using salt elimination and all other procedures, including reverse $[\text{Cp}_2\text{M(NMe}_2)_2/\text{R}_3\text{SiH}]$ amine elimination, failed (166).

7. Oxidative Addition and Elimination

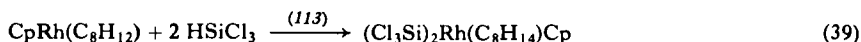
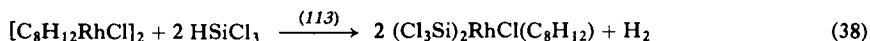
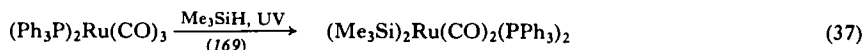
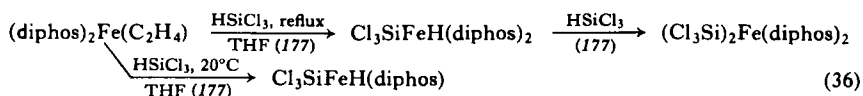
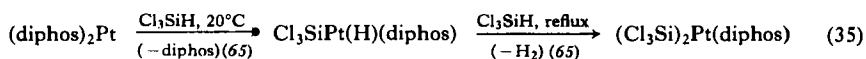
This method (81) has been used for the formation of transition metal bonds to both carbon and silicon, but its range of application reflects the differing bond strengths $\text{M}'\text{—M}'$, $\text{M}'\text{—H}$, and $\text{M}'\text{—X}$ ($\text{M}' = \text{C}, \text{Si}$; $\text{X} = \text{halogen}$) for the two cases. Few additions involving $\text{M}'\text{—M}'$ cleavage are known [$\text{M}' = \text{C}$ (37, 44, 46, 236), Si (215)]. However, for carbon, C—X



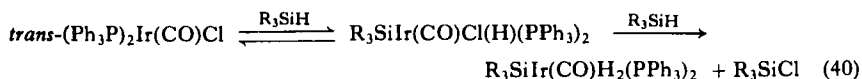
addition is common (81) and C—H cleavage unusual (122, 160, 200, 245) [nearly always, but see (160, 245), involving aromatic C—H]; whereas Si—X addition is unconfirmed {(Ph₃P)₄Ni gives [(Ph₃P)₂NiCl]₂, possibly via Ni—Si intermediates, by reaction with either Ph₃SiCl or HSiCl₃ (see Section II,E,3) (177)} and Si—H cleavage provides a good route to numerous complexes. Such reactions often proceed in high yield under mild conditions and seldom present problems in product separation. Examples are given in Eqs. (25)–(28) (additions) and Eqs. (29)–(34) (eliminations). Oxidative elimination may occur in preference to elimination of hydrogen [e.g., Eq. (34)]. (Further data are in Section III.)

These oxidative reactions are, in general, reversible; stable (even in solution) Si—M adducts are formed when there are electron-withdrawing groups on Si. For addition of (CH₃)_n(C₂H₅O)_{3–n}SiH to [(diphos)₂Ir]⁺BPh₄[–], unequivocal assignment of mechanism was not possible (133); but for the addition of (EtO)₃SiH to (Ph₃P)₃Ir(CO)H, kinetic results are consistent with a unimolecular dissociation of the pentaco-ordinate complex with loss of one molecule of PPh₃, followed by addition of the silane to the square complex so formed (132).

Since these reactions produce transition metal hydrides, hydrogen elimination may occur [Eqs. (35)–(40)] (see Section II,B,4, method b). The intermediate hydride need not be isolated; hydrogen may not be evolved but may react with a ligand [e.g., Eq. (39)], and H/Cl exchange may take place [Eq. (40)]. (Ph₃P)₃Pt reacts with MeCl₂SiH in analogous fashion to Eq. (35) (90) [see also ref. (110a)].



Unexpected products may arise through the great affinity of silicon for halogen [e.g., Eq. (40) ($R = Et, OEt$)] (51).



An oxidative addition step is involved in the reaction between *trans*-(Et_3P)₂Ir(CO)Cl and the mercurials Hg(MMe₃)₂ ($M = \text{Si}, \text{Ge}$) (141).

8. Syntheses from Si—M Precursors

No new silicon-transition metal bonds are formed in these reactions, although new compounds containing such bonds are produced. Details are in Section II,C,1-3.

C. The Reactions of Compounds with Silicon-Transition Metal ($\text{R}_3\text{Si}-\text{M}$) Bonds

The overall stability of the complexes listed in Table II tends to parallel, but exceed, that of their alkyl counterparts. Their chemical reactions may be classified as shown in the headings to Sections II,C,1-5, respectively, of which the Si—M cleavages (Section II,C,3) have been the most studied.

1. Substitution at Silicon

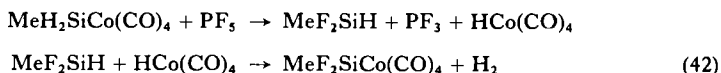
Comparatively few of these reactions are known. It has proved possible to replace the H in H—Si—M by F, Cl, or Br, using PF₅, HCl, or Br₂, respectively; Br in Br—Si—M by Me, using MeLi; and Cl in Cl—Si—M by OR, or NMe₂, using ROH, or Me₂NH, respectively. The Si—M bond must withstand attack by these reagents.

The first example of substitution at Si, a slow gas-phase reaction at 75° C, is shown in Eq. (41) (8, 10); interestingly the Co analog H₃SiCo(CO)₄ gave Si—M cleavage products (9). *trans*-H₂ClSiPtCl(PET₃)₂, with HCl at

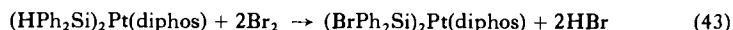


20° C in benzene, gave progressive chlorination to yield finally Cl₃SiPtCl(PET₃)₂; with excess of HCl, there was no further reaction even at 100° C, but the solid complex and liquid HCl gave HSiCl₃ and (Et₃P)₂PtH₂Cl₂ (27).

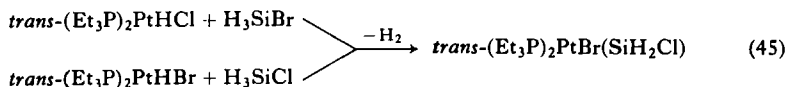
H/F exchange has been observed in a Si—Co system, as shown in Eqs. (42); intermediate Si—Co cleavage was postulated and hydrides $\text{HCo}(\text{CO})_n(\text{PF}_3)_{4-n}$ were also obtained (116, 117).



Bromination and alkylation are illustrated in Eqs. (43) and (44) (65).

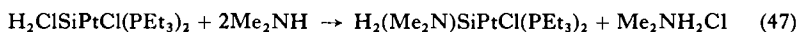
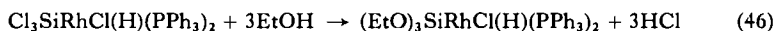


Cl/Br exchange at Si is indicated from Eq. (45) (27).



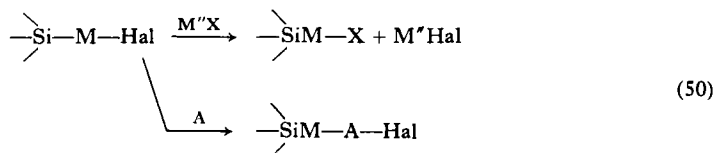
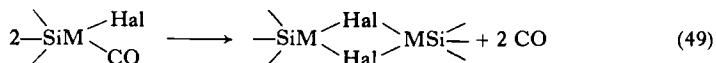
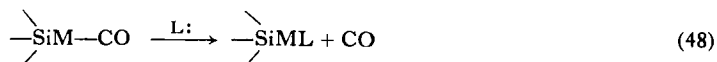
In toluene at -60°C the NMR spectrum of a mixture of H_3SiBr and $\text{trans}-(\text{Et}_3\text{P})_2\text{PtHCl}$ showed that all of the H_3SiBr is converted into H_3SiCl prior to formation of a Si—Pt product.

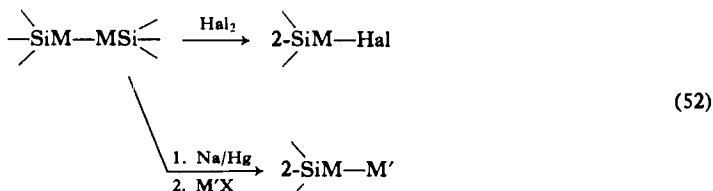
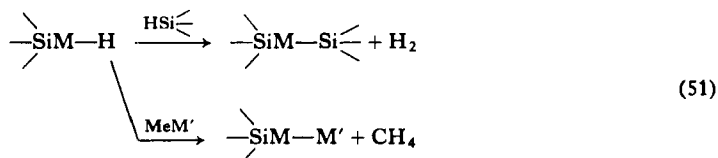
Alcoholysis [e.g., Eq. (46) (135)] and aminolysis [e.g., Eq. (47) (27)] experiments have been carried out.



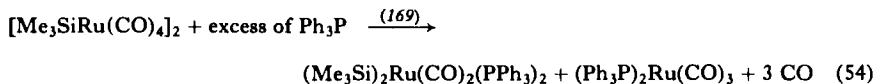
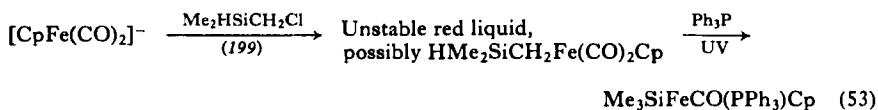
2. Substitution at the Transition Metal

Substitution reactions at the transition metal M involve displacement of neutral (CO) or anionic (halide, hydride, or metallate) ligands, as summarized in Eqs. (48)–(52).





Whereas alkyl transition metal complexes often undergo CO insertion by treatment with CO or (for carbonyls) other neutral ligands such as phosphines (45, 137), such reactions are not reported for Si—M compounds (9, 10, 218). Displacement of 1 or, rarely, 2 moles of CO by R_3P [Eq. (48)] is known for $\text{R}'_3\text{SiCo}(\text{CO})_4$ ($\text{R}' = \text{H}$, with $\text{R} = \text{Ph}$; $\text{R}' = \text{Cl}$, Et , with $\text{R} = \text{Et}$) (9, 156), $\text{R}'_3\text{SiM}(\text{CO})_4$ ($\text{R}' = \text{F}$, Ph , C_6F_5 , with $\text{R} = \text{Ph}$ and $\text{M} = \text{Mn}$; $\text{R}' = \text{F}$, with $\text{R} = \text{Ph}$ and $\text{M} = \text{Re}$) (217, 218), $\text{Me}_3\text{SiMn}(\text{CO})_4$ ($\text{R} = \text{F}$) (31), $\text{Me}_3\text{SiFe}(\text{CO})_2\text{Cp}$ (163), and $(\text{Me}_3\text{Si})_2\text{Ru}(\text{CO})_4$ (169). $\text{R}'_3\text{SiRe}(\text{CO})_5$ ($\text{R}' = \text{Ph}$, C_6F_5) did not react with Ph_3P even at 160°C (217). Alternative routes to two of the substitution products are shown in Eqs. (53) and (54). By contrast to Eq. (54), $[\text{Cl}_3\text{SiRu}(\text{CO})_4]_2$ did not react with Ph_3P (169).



Reactions of the type shown in Eq. (49) are established for the conversion of $\text{Me}_3\text{SiM}(\text{CO})_4\text{X}$ ($\text{M} = \text{Ru}$, Os ; $\text{X} = \text{Br}$, I) to $[\text{Me}_3\text{SiM}(\text{CO})_3\text{X}]_2$ (6).

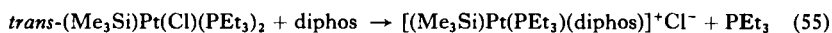
The displacement reactions of Eq. (50) have been demonstrated *inter alia* for $(\text{EtO})_3\text{SiRhCl}(\text{H})(\text{PPh}_3)_2/\text{LiBr}$ (135), *trans*- $\text{Ph}_3\text{SiPtCl}(\text{AsMe}_2\text{Ph})_2/\text{NaN}_3$ (64), *trans*- $\text{Me}_3\text{SiPtCl}(\text{PEt}_3)_2/\text{LiGePh}_3$ (114), and $\text{Me}_3\text{SiRu}(\text{CO})_3\text{---}(\text{PPh}_3)\text{I}/\text{NaBH}_4$ (to give the hydride) (6). The insertion reactions are

established for *trans*-Ph₃SiPtX(PMe₂Ph)₂/SnX₂ (X = Cl, Br) and /InCl (64), and Me₃SiOs(CO)₄H/C₂F₄ (170).

A number of hydrogen elimination reactions [Eq. (51)] from SiM precursors were discussed in Section II,B,4; another example is that from Cl₃SiRhCl(H)(PPh₃)₂/HSiCl₃ (135). The methane elimination is established for Me₃SiOs(CO)₄H/MeAuPPh₃ (168).

Halogen may cause substitution at Si (Section II,C,1) or Si—M cleavage (Section II,C,3). However, substitution at M [Eq. (52)] was demonstrated for [Me₃SiM(CO)₄]₂/X₂ systems (M = Ru, Os; X = Br, I) (6). Reduction of [Me₃SiRu(CO)₄]₂ by sodium amalgam affords [Me₃SiRu(CO)₄][−]Na⁺, which is a convenient source for SiM—metal-bonded compounds [in Eq. (52) M' = SnMe₃, SnPh₃, GeBu₃, Mn(CO)₅, or AuPPh₃; and X = Cl or Br] (169).

A combination of neutral and anionic ligand displacements is shown in Eq. (55) (115); it was suggested that the high *trans* influence of Me₃Si leads to Pt—Cl bond weakening and hence the ionic product rather than *cis*-Me₃SiPtCl(diphos) [which is a stable compound (69, 71)].



3. Cleavage of the Silicon–Transition Metal Bond

a. *Cleavage by Protic Species.* A few solvolyses at silicon have already been mentioned (Section II,C,1). In general, however, such reactions proceed with cleavage of the Si—M bond. Reports of hydrolytic stability should be viewed with caution, since apparent inertness may originate through the substrate not being wetted by water. Thus, 80% of Me₃SiMn(CO)₅ was recovered after 24 hours in suspension in water at 20° C, whereas only 9% was recovered after 5 minutes in aqueous ethereal solution at 20° C (31); the hydrolysis products were (Me₃Si)₂O and 2HMn(CO)₅. Some silylrhodium complexes can be dissolved in hydroxylic solvents without cleavage of the Rh—Si bond; but Me₃SiRhCl(H)(PPh₃)₂, which dissociates in solution, is cleaved in aqueous diglyme [Eq. (56)] (135).

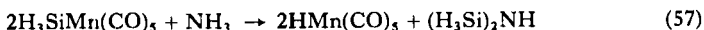


Similar hydrolyses were observed with Me₃SiCo(CO)₄ (182) and *trans*-Me₃SiPt(Cl)(PEt₃)₂ (114), although silane was the only observed volatile product from H₃SiM(CO)₃Cp (M = Cr, Mo, W) (124). Whereas the above platinum complex was hydrolyzed instantly, the ionic analog [Me₃SiPt(PEt₃)(diphos)]⁺Cl[−] underwent only 30% reaction after 50 days

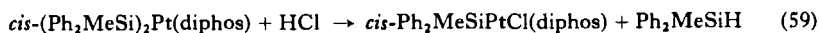
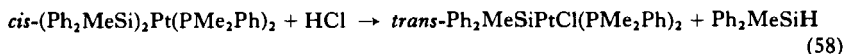
under the same conditions (aqueous diglyme). The rate-determining step was believed to be electrophilic attack at Pt (containing most of the positive charge in the cationic species) rather than nucleophilic attack at Si (115). *trans*-Me₃SiPt(GePh₃)(PET₃)₂ reacted rapidly with water, with preferential cleavage of the Si—Pt rather than the Ge—Pt bond (114).

(H₃Si)₂Fe(CO)₄ hydrolyzed fairly rapidly (12). Me₃SiFe(CO)₂Cp was recovered unchanged after 1 hour in aqueous ether, but was decomposed by methanolic KOH (191a). Homogeneous and quantitative methanolysis of Me₃SiM(CO)_n (M = Mn, *n* = 5; M = Co, *n* = 4) to give Me₃SiOMe, occurred rapidly at 20° C (13, 182). Treatment of Ph₃SiPtCl(PMe₂Ph)₂ with PhSH furnishes (Me₂PhP)₂Pt(SPh)₂, (Me₂PhP)₂PtCl₂, and Ph₃SiH (63).

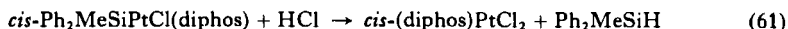
Ammonia undergoes a complex reaction with H₃SiCo(CO)₄; the Si—Mn bond in H₃SiMn(CO)₅ was quantitatively cleaved according to Eq. (57) (11). Me₃SiCo(CO)₄ reacts analogously with Me₂NH at 20° C to give HCo(CO)₄ and Me₃SiNMe₂ (14).



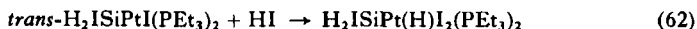
In platinum chemistry, cleavage of bis(silyl) compounds by HCl may be used [Eqs. (58), (59)] to generate monosilyl complexes (63).



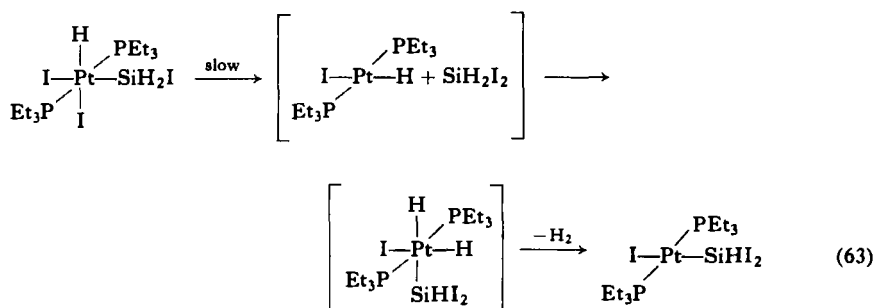
However, different reactions occur with a further mole of HCl [Eqs. (60), (61)].



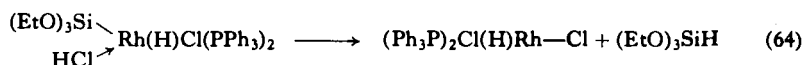
The change in the group trans to the silyl ligand is thought to account for the reversal of substitution pattern in the case of the monodentate phosphine (63). Six-coordinate Pt(IV) intermediates have been postulated for these Pt(II) reactions (27, 71). Such an intermediate has recently been isolated [Eq. (62)] (27).



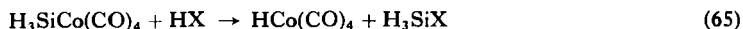
This yellow crystalline Pt(IV) complex decomposes slowly at 20° C with evolution of hydrogen and formation of *trans*-HI₂SiPtI(PET₃)₂. The proposed mechanism is shown in Eq. (63).



A Rh—Si bond cleavage has been demonstrated, but an addition-elimination mechanism is unlikely as this would require a seven-coordinate Rh(V) intermediate; coordination of HCl through the chlorine atom was postulated [Eq. (64)] (135).



The reactivity sequence $\text{Co} > \text{Fe} > \text{Mn}$ has been established for $\text{H}_3\text{SiM}(\text{CO})_n$: thus, whereas $\text{H}_3\text{SiCo}(\text{CO})_4$ was readily cleaved [according to Eq. (65) ($\text{X} = \text{Cl}, \text{F}$)] (9), $(\text{H}_3\text{Si})_2\text{Fe}(\text{CO})_4$ was only 9% decomposed [Eq. (66)] after 10 minutes at just above room temperature (12), and $\text{H}_3\text{SiMn}(\text{CO})_5$ did not react with HCl at room temperature (10).

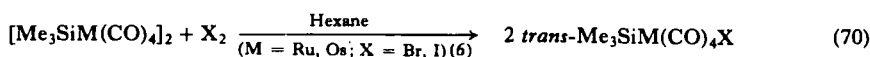
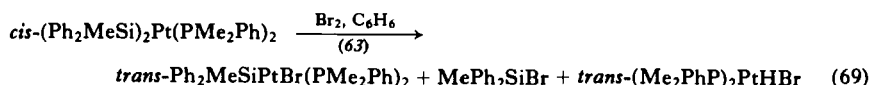
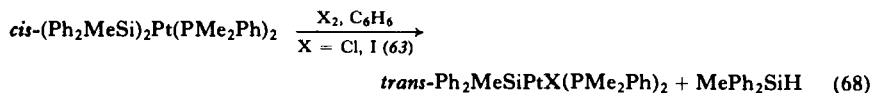


The inertness of $\text{H}_3\text{SiMn}(\text{CO})_5$ contrasts with the reactivity of its pyridine adduct $\text{H}_3\text{SiMn}(\text{CO})_5 \cdot 2\text{C}_5\text{H}_5\text{N}$, which was decomposed quantitatively below -100°C [Eq. (67)] (11), (but see Section II,C,4).

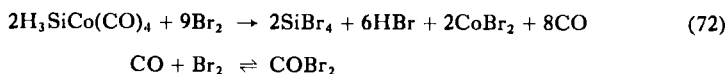


The reaction of *trans*-(Me_3Si)₂Os(CO)₄ with HCl gave *trans*-Cl₂Os(CO)₄ (43); $\text{H}_3\text{SiM}(\text{CO})_3\text{Cp}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) gave $\text{HM}(\text{CO})_3\text{Cp}$ and H_3SiCl (124). $\text{Ph}_3\text{SiZr}(\text{Cl})\text{Cp}_2$ and HCl gave Cp_2ZrCl_2 and Ph_3SiH , whereas the hafnium analog and HBr gave Ph_3SiH and $\text{Cp}_2\text{Hf}(\text{Br})\text{Cl}$ (166). Reference should also be made to Section III.

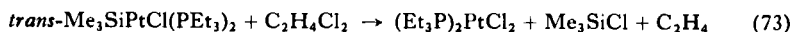
b. *Cleavage by Halogens and Chloroalkanes.* The halogens have not been extensively investigated as cleavage reagents. Some examples are given in Eqs. (68)–(71).



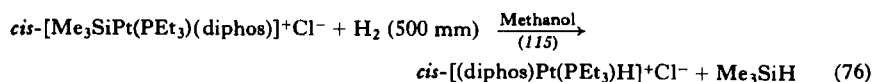
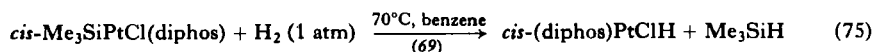
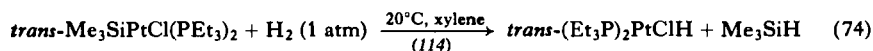
Bromine caused complete destruction of $\text{H}_3\text{SiCo}(\text{CO})_4$ [Eqs. (72)] (9).



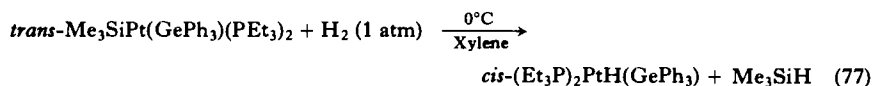
1,2-Dichloroethane acts as a mild chlorinating agent towards *trans*- $\text{Me}_3\text{SiPtCl}(\text{PEt}_3)_2$ [Eq. (73) (114)], and CDCl_3 caused the conversion of $\text{Ph}_3\text{SiZr}(\text{Cl})\text{Cp}_2$ into Cp_2ZrCl_2 (166).



c. *Cleavage by Hydrogen.* The homogeneous hydrogenolysis of compounds with Pt—Group IVB element bonds has been examined [cf., ref. (71) and references therein]. For Pt complexes $(\text{R}_3\text{M}')_2\text{Pt}(\text{PR}'_3)_2$ ($\text{M}' = \text{Si, Ge, Sn, Pb}$) only one Pt— M' bond is readily cleaved, to afford $\text{R}_3\text{M}'\text{PtH}(\text{PR}'_3)_2$ (71). Some chelate phosphine complexes of the type $(\text{Ph}_3\text{M}')_2\text{Pt}(\text{chelate})$ behave similarly but require a higher pressure of hydrogen. Other monosilylplatinum(II) compounds are readily hydrogenolysed, as shown in Eqs. (74)–(76). Quantitative and preferential

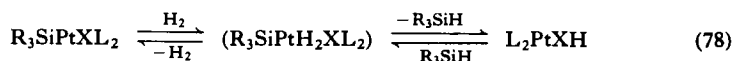


cleavage of the Pt—Si bond in a mixed complex occurred rapidly at 0° C

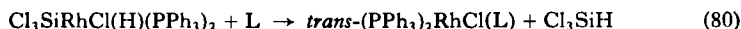


[Eq. (77)] (114). The reaction of $(\text{Me}_3\text{Si})_2\text{Pt}(\text{diphos})$ with hydrogen in benzene at atmospheric pressure affords $\text{Me}_3\text{SiPtH}(\text{diphos})$ at 40° C and $(\text{diphos})_3\text{Pt}_4$ at 80° C (71). Kinetic studies showed that the reaction is first order in hydrogen and in the platinum complex ($k_2 = 4.1 - 6.0 \times 10^{-2}$ mole⁻¹ second⁻¹ at 25° C in toluene), consistent with a mechanism involving oxidative addition of hydrogen to platinum followed by elimination of Me_3SiH .

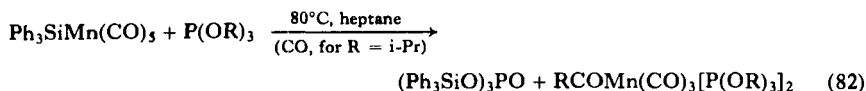
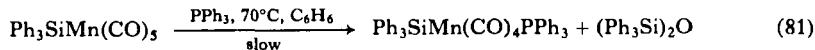
The reversible hydrogenolysis of *trans*-(Ph_2MeSi)₂Pt(PMe₂Ph)₂ has been discussed in Sections II,B,4 and II,B,7. A mechanism similar to that postulated for hydrogen halide reactions [e.g., Eq. (78)] has been suggested (71, 114); such a dihydride intermediate has not been detected, but some support comes from the identification of $\text{H}_2\text{XSiPtI}_2(\text{H})(\text{PEt}_3)_2$ (X = Cl, I), as shown in Eq. (79) (27). Further discussion is in Section III.



d. *Cleavage by Neutral Ligands.* Oxidative addition of $\text{H}-\text{Si} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix}$ to transition metal complexes is reversible (Sections II,B,7 and III). The Si—M complex may dissociate (reductive elimination) in solution [e.g., $(\text{EtO})_3\text{SiIrH}(\text{CO})\text{Cl}(\text{PPh}_3)_2$ (55)], or although stable in solution may react with stronger ligands to displace the silane [e.g., Eq. (80) (L = CO, PF₃, C₂H₄) (135)]. Transmetallation (Section II,C,3,e) is a special case of Eq. (80), with L = covalent halide or hydride.

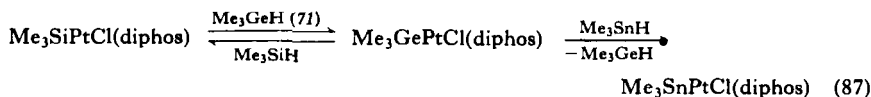
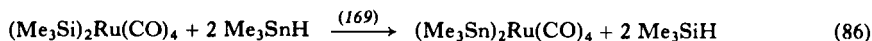
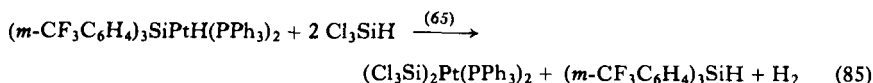
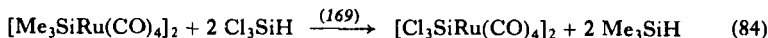
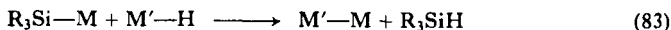


In cases where a simple reductive elimination cannot take place, Si—M cleavage may still occur, as shown in Eqs. (81) (217) and (82) (R = Me, *i*-Pr, Ph) (103, 207). When the reaction of $\text{Ph}_3\text{SiMn}(\text{CO})_5$ with PPh_3 was carried out at 130° C in decalin, only the substitution product $\text{Ph}_3\text{SiMn}(\text{CO})_4\text{PPh}_3$ was observed (103, 207).



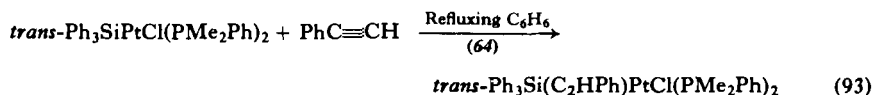
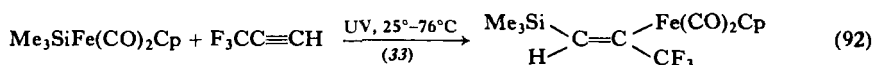
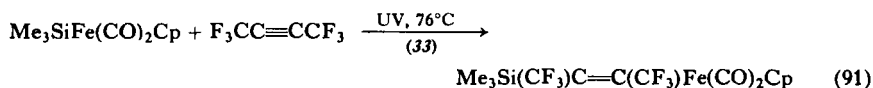
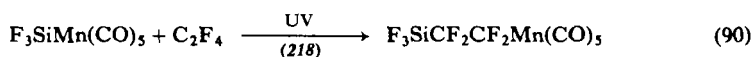
Attempts to synthesize a π -silacyclopentadienyl derivative from $\text{C}_4\text{Ph}_5\text{Si-Fe(CO)}_2\text{Cp}$ by heating or UV irradiation, failed (91).

e. *Transmetallations Involving Silicon.* Transmetallations involving silyl ligands may occur in reactions with covalent halides or hydrides [e.g., Eq. (83)]. In some cases one silyl group may be replaced by another ($\text{M}' = \text{a Si ligand}$) (giving an indication of relative ligand strengths) or other metal-metal bonds (e.g., $\text{M}' = \text{Ge, Sn, Hg}$) may be formed. In general, Ge and Sn ligands displace Si ligands (71, 169); examples are given in Eqs. (84)–(89). Measurements of $\text{M}'\text{-M}$ ($\text{M}' = \text{Ge or Sn}$; and $\text{M} = \text{Cr, Mo, or W}$) bond dissociation energies show that bond strengths decrease in the series $\text{Sn} > \text{Ge}$ and $\text{W} > \text{Mo} > \text{Cr}$ for $\text{Me}_3\text{M}'\text{-M(CO)}_3\text{Cp}$ (49). $\text{Ph}_3\text{SiZr(Cl)Cp}_2$ and HgCl_2 gave Cp_2ZrCl_2 , Ph_3SiCl , and Hg (166).



f. *Insertions into the Si-M Bond.* Although insertions of unsaturated species into carbon-metal or metal-metal bonds are well known [see ref. (73)], there are comparatively few examples in Si-M chemistry. No case of insertion of CO (Section II,C,2) or SO_2 {with $\text{R}_3\text{SiMn(CO)}_5$ [$\text{R} = \text{H}$ (10), F (218)] or $\text{Me}_3\text{SiFe(CO)}_2\text{Cp}$ (34)} is known. Insertions of fluoroolefins or acetylenes have, however, been demonstrated [e.g., Eqs. (90)–(93)], but such

reactions are evidently not widely applicable. A reaction of $\text{Me}_3\text{SiFe}(\text{CO})_2\text{Cp}$ with perfluorocyclobutene gave only a low yield of $[\text{CpFe}(\text{CO})_2]_2$ (33). In



Eq. (93), the phenylacetylene appears to have inserted into the Si—Pt bond to give a substituted vinyl complex, but its exact structure was not established. Under the conditions used for $\text{PhC}\equiv\text{CH}$, no reaction was observed between the same SiPt complex and tolan, cyclohexene, styrene, acrylonitrile, or benzaldehyde; tetracyanoethylene reacted very rapidly, but the oil formed was not crystallized (64). In contrast, reaction of $\text{PhC}\equiv\text{CH}$ with *trans*- $\text{Me}_3\text{SiPtCl}(\text{PEt}_3)_2$ did not give insertion products but instead the complexes $(\text{Et}_3\text{P})_2\text{PtCl}(\text{C}\equiv\text{CPh})$, $(\text{Et}_3\text{P})_2\text{PtH}(\text{C}\equiv\text{CPh})$, $(\text{Et}_3\text{P})_2\text{Pt}(\text{C}\equiv\text{CPh})_2$, as well as a compound of empirical formula (mass spectrometry) $(\text{Et}_3\text{P})_2\text{PtCl}(\text{SiMe}_3\text{Ph}_2\text{C}_2\text{H}_4)$ (114).

4. Addition at Silicon

Tertiary amines are known to form adducts with H_3Si derivatives of iron (12), cobalt (11), and manganese (11). Pyridine and trimethylamine formed 1:2 adducts in all cases, while 2,2'-bipyridyl gave 1:1 adducts with $\text{H}_3\text{SiCo}(\text{CO})_4$ and $\text{H}_3\text{SiMn}(\text{CO})_5$. The complex $\text{H}_3\text{SiCo}(\text{CO})_4 \cdot 2\text{py}$ was considerably more thermally stable than its parent compound, while $\text{H}_3\text{SiMn}(\text{CO})_5 \cdot 2\text{py}$ showed greatly enhanced reactivity toward HCl (Section II,C,3,a). The cobalt adducts were the most stable, but only $\text{H}_3\text{SiCo}(\text{CO})_4 \cdot 2\text{NMe}_3$ showed reasonable inertness to air. The IR spectra of the manganese and cobalt adducts in the carbonyl region showed a strong band assigned to the carbonyl-metallate anion. Thus, they are formulated as $[\text{H}_3\text{Si} \cdot 2\text{Base}]^+\text{M}(\text{CO})_n^-$ in the solid state, and might appropriately have been considered in Section II,C,3 (Si—M cleavage). Although there are

potentially two silicon acceptor sites in $(\text{H}_3\text{Si})_2\text{Fe}(\text{CO})_4$, only a 1:2 adduct was formed with triethylamine. An HCl cleavage experiment suggested that both acceptor sites are singly coordinated. An adduct was originally formulated as $[\text{H}_3\text{Si} \cdot n\text{NMe}_3]^+[\text{HFe}(\text{CO})_4]^-$ (12); an alternative seems likely following the identification of $[\text{Et}_3\text{NH}]^+[\text{Ph}_3\text{SiFe}(\text{CO})_4]^-$ (152). The complexes $\text{H}_3\text{SiM}(\text{CO})_3\text{Cp}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) form adducts with Me_3N and Me_2NH ; $\text{Si}-\text{M}$ cleavage occurs on heating the dimethylamine derivatives (124).

Adduct formation has been observed with trialkylsilylcobalt complexes to give $[\text{R}_3\text{SiB}]^+[\text{Co}(\text{CO})_4]^-$ (where $\text{R} = \text{Me}$ and $\text{B} = \text{NMe}_3, \text{PMe}_3, \text{PEt}_3$; $\text{R} = \text{Et}$ and $\text{B} = \text{PEt}_3$) (17). No formation of substituted ammonium or phosphonium salts was observed when electronegative groups were attached to silicon or phosphorus.

5. Addition at the Transition Metal

The complexes $\text{R}_3\text{SiRhX(H)}(\text{PPh}_3)_2$, assumed from NMR data to be trigonal bipyramidal and shown to be so in one case by X-ray diffraction (see Section II,D), are coordinatively unsaturated and might be expected to take up a further ligand. Recrystallization of compounds ($\text{X} = \text{Cl}, \text{Br}$; $\text{R} = \text{OEt}$) in the presence of a large excess of Ph_3P gave no suggestion of products containing additional coordinated ligands. When other phosphines (e.g., Ph_2MeP) were used, only ligand replacement occurred. However, reaction of a solid complex ($\text{X} = \text{Cl} = \text{R}$) with CO or PF_3 did give (IR for CO adduct) the impure six-coordinate derivatives; whereas, when the process was carried out in solution, the trichlorosilane was displaced by the incoming nucleophile (Section II,C,3,d) (135).

D. Structure and Bonding

In addition to routine spectroscopic characterization, transition metal silyls have been examined by a variety of physical methods, principally to determine (1) the definite presence of an $\text{Si}-\text{M}$ bond, (2) the manner in which such a bond is influenced by other ligands, (3) whether such a bond possesses any π -component, and (4) the trans influence of the silyl ligand.

1. Diffraction Studies

Eight diffraction studies have to date been published on compounds having $\text{R}_3\text{Si}-\text{M}$ bonds. Details are in Table IV. In order to assess the

TABLE IV
SELECTED DISTANCES AND ANGLES FOR SILICON-TRANSITION METAL COMPLEXES

Compounds	M—Si (obs.) (Å)	M—Si (calc.) (Å)	M—Si (Pauling) (Å)	Si—X (Å)	M—Si—X (deg)	X—Si—X (deg)	References
Me ₃ SiMn(CO) ₅	2.497(5)	2.63	2.34	1.91(2)	—	—	127
(Cl ₃ Si) ₂ Fe(H)(CO)Cp	2.252(3)	2.51	2.34	2.052(3)	115(8)	104(3)	184
H ₃ SiCo(CO) ₄	2.381(7)	2.51	2.34	—	—	—	205
F ₃ SiCo(CO) ₄	2.226(5)	2.51	2.34	1.51(1)	115(5)	104(7)	109
Cl ₃ SiCo(CO) ₄	2.254(3)	2.51	2.34	2.035(3)	113(13)	105(14)	206
Cl ₃ SiRh(H)(Cl)(PPh ₃) ₂	2.203(4)	2.48	2.43	2.054(6)	109–121	102(3)	191
<i>trans</i> -Ph ₂ MeSiPt(Cl)(PMe ₂ Ph) ₂	2.29	—	2.46	—	—	—	188
Cp ₂ ZrCl(SiPh ₃)	2.813(2)	—	2.63	1.913(4)	110–119	105.5 (mean)	190

significance of the derived Si—M bond lengths, there is ambiguity about the choice of appropriate covalent radii, because of the uncertainty in deciding in what way the transition metal radius in a specific compound is influenced by features such as stereochemistry of the complex and the oxidation state and coordination number of the metal (179). A series of approximate Si—M single-bond lengths has been proposed, derived from (1) transition metal radii calculated from data on other binuclear species and (2) the Pauling covalent tetrahedral radius of silicon (1.17 Å) (184). From Table IV it is clear that the observed Si—M distances are, with one exception, shorter than the calculated values by 0.13–0.28 Å. The shortening is greatest when the silyl ligand carries electronegative substituents such as Cl or F. However, from the near equivalence of the Co—Si distances in $F_3SiCo(CO)_4$ (109) and $Cl_3SiCo(CO)_4$ (106), it appears that this shortening is not purely a function of electronegativity (e.g., because of contraction of the Si d orbitals by a strongly electron-withdrawing ligand), but is in part caused by ($d-d$) π -bonding. Consistent with this view, by far the longest Si—M distance is found in a Zr(IV), a d^0 , complex (190). For $Cl_3SiRhCl(H)-(PPh_3)_2$, the only other complex containing a silyl group bound to a second-row transition metal for which data are available, the Si—Rh bond length is 0.61 Å shorter (191). Evidence for π -bonding in Rh(III) and Pt(II) silyls was provided by comparing M—Si and M—C bond lengths for M = Zr(IV), Rh(III), and Pt(II) (166).

For a series of complexes ML_2Cl_4 and ML_3Cl_3 (where L is a tertiary phosphine and M a third-row transition metal) comparable M—P bond lengths decrease by 0.05 Å as the number of metal d electrons is increased by one; these results are interpreted in terms of a regular decrease of the metal σ -bond radius as the third transition series is traversed (6a). If a similar trend exists in the second transition series, then only about one-half of the 0.61 Å difference between the Zr—Si and Rh—Si bond lengths can be accounted for in terms of the differing σ -bond radii of Zr(IV) (d^0) and Rh(III) (d^6). Hence either Si—M ($d-d$) π bonding (negligible with the d^0 Zr complex) is important for the d^6 complex, or the Rh—Si and Zr—Si bonds are different in nature (e.g., in ionic character) (190). The significance of the latter possibility in particular instances may be illustrated by comparison of the d^6 $Cl_3SiRhCl(H)(PPh_3)_2$ (191) with the ruthenium compounds $Ph_3PRuCl(X)(PPh_3)_2$ [X = H (222), Cl (176)]. All three structures are best considered as trigonal bipyramids with two apical phosphine ligands trans to one another and a short contact between a phenyl hydrogen and M. The

mean distance between the two apical P atoms and M is normal in all cases [2.338(4) Å (Rh), 2.345(4) Å (Ru, X = H), 2.393(6) Å (Ru, X = Cl)], but in the Ru complexes the third (equatorial) P is much nearer to M [2.206(4) Å (X = H), 2.230(8) Å (X = Cl)]. It is this equatorial phosphine which is situated in an analogous position to that of the Cl_3Si ligand in the Rh complex, where the Si—M distance [2.203(4) Å] is the shortest yet found. These short distances are presumably due to the absence of competing π -acceptor ligands in a trans position. The data suggest that the Cl_3Si group is a better acceptor than Ph_3P , because the covalent radii of Rh and Ru are approximately equal, whereas the radius of phosphorus is some 0.07 Å shorter than that of silicon (191). In $(\text{Cl}_3\text{Si})_2\text{Fe}(\text{CO})\text{HCp}$, the Cl_3Si ligands are trans to each other with an Fe—Si distance of 2.252(3) Å (184).

The crystal structure of *trans*- $\text{Ph}_2\text{MeSiPtCl}(\text{PMe}_2\text{Ph})_2$ has revealed an unexceptional Pt—Si bond length of 2.29 Å, but the length of the Pt—Cl bond trans to the silyl group is 2.45(1) Å: This is the longest recorded for any Pt(II) complex and is taken as indicative of the large trans influence of the silyl ligand (138) (see also Sections II,D,2 and 3).

The structures of $\text{Cl}_3\text{SiCo}(\text{CO})_4$ (206), $(\text{Cl}_3\text{Si})_2\text{FeH}(\text{CO})\text{Cp}$ (184), and $\text{Cl}_3\text{SiRhH}(\text{Cl})(\text{PPh}_3)_2$ (191) are illustrated in Figs. 1–3.

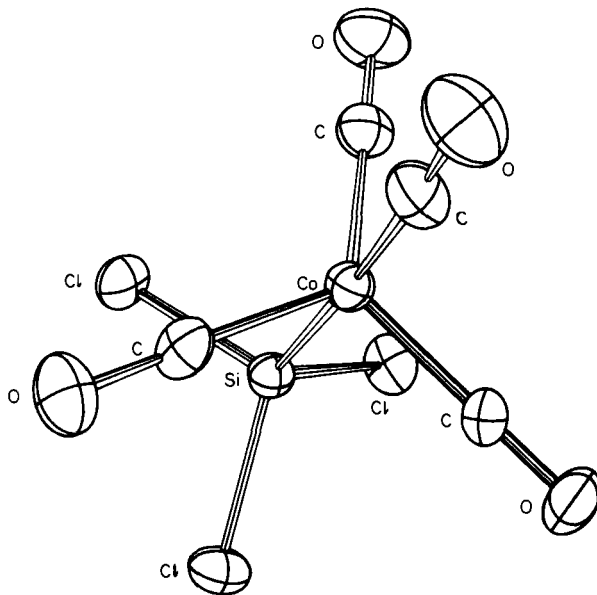


FIG. 1. A perspective drawing of $\text{Cl}_3\text{SiCo}(\text{CO})_4$.

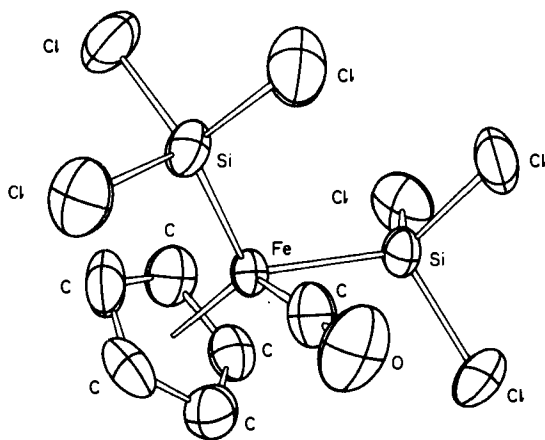


FIG. 2. A perspective view of the structure of $(\text{Cl}_3\text{Si})_2\text{Fe}(\text{CO})(\text{H})\text{Cp}$.

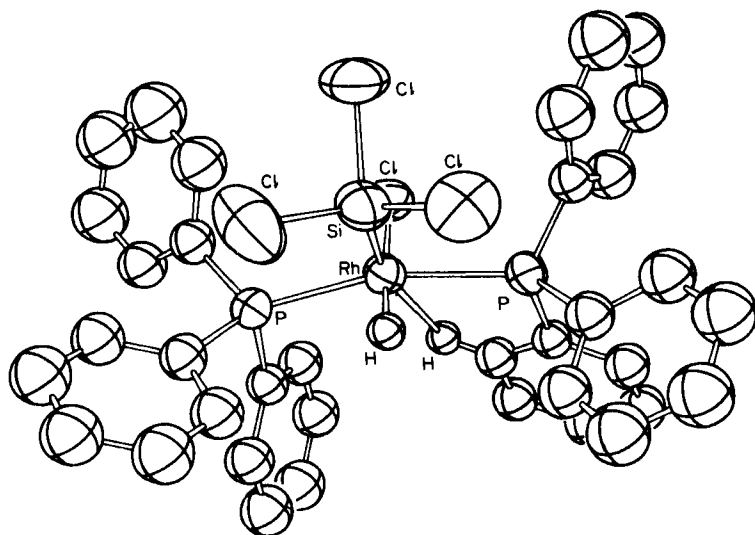


FIG. 3. A perspective view of the structure of $\text{Cl}_3\text{SiRh}(\text{H})(\text{Cl})(\text{PPh}_3)_2$. (There is a close *o*-H/Rh contact.)

2. IR and Raman Studies

Vibrational spectroscopy has generally been applied to Si—M complexes in order to assign Si—M, M—Cl, M—P, or M—CO stretching mode(s).

Assigned Si—M stretching modes are listed in Table V; $\nu(\text{Si—M})$ is at $\sim 300 \text{ cm}^{-1}$. This indicates stretching force constants of about 1–2 mdyne \AA^{-1} , using a simple SiM diatomic approximation. The procedure has been used to predict the location of $\nu(\text{Group IV element—M})$ (38, 134) and gives Si—M stretching force constants which differ little from Ge—M and Sn—M analogs (38, 159); however, agreement with experiment is better if the

TABLE V
Si—M STRETCHING FREQUENCIES FOR SILICON—TRANSITION
METAL COMPLEXES

Compounds	$\nu(\text{Si—M})$ (cm^{-1})	References
$\text{H}_3\text{SiMn}(\text{CO})_5$	302	10
$\text{Me}_3\text{SiMn}(\text{CO})_5$	293	157
$\text{Cl}_3\text{SiMn}(\text{CO})_5$	291	157
$\text{H}_3\text{SiCo}(\text{CO})_4$	310	9
$\text{Me}_3\text{SiCo}(\text{CO})_4$	295	157
$\text{Cl}_3\text{SiCo}(\text{CO})_4$	303	157
<i>trans</i> - $\text{Me}_3\text{SiPt}(\text{Cl})(\text{PEt}_3)_2$	352	114
<i>trans</i> - $\text{Me}_3\text{SiPt}(\text{GePh}_3)(\text{PEt}_3)_2$	337	114
$\text{Ph}_3\text{SiAuPPh}_3$	305	15

masses of the attached ligands are also considered (49). There are at present insufficient data to enable any correlation between $\nu(\text{M—Si})$ and the nature of the ligands attached to silicon to be established, although this has been achieved in the tin series $\text{Me}_{3-n}\text{Cl}_n\text{SnMn}(\text{CO})_5$, $n = 0-3$ (50); assignments of $\nu(\text{M—Si})$ are available for $\text{X}_3\text{SiM}(\text{CO})_n$ ($\text{X} = \text{Cl}$ or Me , $\text{M} = \text{Co}$, $n = 4$; $\text{M} = \text{Mn}$, $n = 5$) (157). Of the two listed SiPt(II) compounds, the lower value of $\nu(\text{Pt—Si})$ in *trans*-(Me_3Si)Pt(GePh_3)(PEt_3)₂ is consistent with a trans labilizing order $\text{Ph}_3\text{Ge} > \text{Cl}$ (114).

Most treatments of CO stretching force constants in SiM carbonyls use the Cotton-Kraihanzel model (85), in which differences ($k_2 - k_1$) between the force constant (k_1) of the CO ligand trans to the silyl group and that (k_2) of the equatorial *cis* CO ligand are considered to reflect the degree of π -character present in the SiM bond. Although this was not originally (85) regarded as applicable to trigonal bipyramidal molecules, the method was

used for SiCo (125). For Cl_3SiMn and Cl_3SiRe complexes, it was suggested that there was strong π -bonding (as for the GeM and SnM analogs) (148, 153). This approach to π -bonding has been criticized (205) and extensions suggested (100). In a study of a large range of Group IVB metal carbonyl derivatives, the earlier emphasis placed on ($d-d$) π -bonding is questioned and a significant σ -inductive effect is suggested (90, 119). The position of $\nu(\text{CO})$ in some SiMn compounds has been interpreted in terms of a π -acceptor capacity (C_6F_5)₃Si > Ph₃Si and F_3Si > F_3C (217, 218). Recent work involves silyl complexes of Fe (12, 97, 99), Mn (100, 154), and Re (100).

The occurrence of more than two $\nu(\text{CO})$ bands in the IR spectrum of $\text{Cl}_2\text{MeSiFe(CO)}_2\text{Cp}$ has led to the suggestion that conformational or rotational isomers are present, and the simple NMR spectrum is explained by assuming rapid interconversion of the two species (148). Assignments of particular $\nu(\text{CO})$ bands to the corresponding conformers have been made on the basis of $\nu(^{13}\text{CO})$ studies (93, 93a). A similar situation has been observed in the analogous Sn and Ge compounds, and, in the latter, two of the four CO bands disappear at -40°C in agreement with the postulate (193).

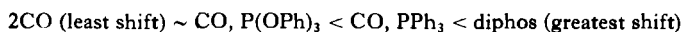
trans-Phosphine complexes of Pt(II) usually show one $\nu(\text{Pt}-\text{P})$ at 418–400 cm^{-1} , whereas *cis* isomers exhibit a doublet at 440–425 cm^{-1} (2). This has been used to assign *trans* configurations to $\text{Me}_3\text{SiPtX(PEt}_3)_2$ ($\text{X} = \text{Cl, GePh}_3$) (114). Tentative assignments for $\nu(\text{Pt}-\text{P})$ and $\nu(\text{Pt}-\text{As})$ in some aromatic SiPt compounds have been made (63).

The location (63, 114) of Pt—X stretching frequencies in *trans*-(R_3Si)₂PtX(QR₃) ($\text{X} = \text{Cl, Br; Q} = \text{P, As}$), has provided information on the *trans* influence of silyl ligands (63), assuming reasonably pure Pt—X modes (136). When *trans* to Cl, such groups cause a marked lowering of $\nu(\text{Pt}-\text{Cl})$ and give rise to the lowest recorded Pt—Cl stretching frequencies. Furthermore, the lowest values are found with electron-releasing substituents at Si.

3. NMR Studies

^{29}Si ($I = \frac{1}{2}$) NMR spectra of SiM complexes have not yet been reported. However, $^1\text{H}-^{29}\text{Si}$ coupling has been observed, for example, in the ^1H NMR spectrum of the strong acid $(\text{Cl}_3\text{Si})_2\text{Fe(CO)HCp}$ (151). NMR techniques have routinely been applied in SiM chemistry for the assignment of stereochemistry [e.g., for ^1H (27, 63, 64, 114, 115), and ^{31}P (136)], and the study of exchange processes [e.g., (27, 174)]. Other data have been interpreted in terms of electronic effects associated with the silyl ligand, but arguments based on chemical shifts must be treated with reservation.

For $\text{Me}_3\text{SiFe}(\text{CO})(\text{PR}_3)\text{Cp}$, the Cp ^1H shifts are to higher field compared with the unsubstituted $\text{Me}_3\text{SiFe}(\text{CO})_2\text{Cp}$, in agreement with transfer to the Cp ring of increased electron density through substitution of CO by the weaker π -acceptor R_3P (163). However, such shifts are essentially independent of phosphine ligand, although chemical shift changes are observed for the $-\text{SiMe}_3$ protons. This may be due to saturation in the Cp ring anti-bonding orbitals, excess charge on the metal passing into the $-\text{SiMe}_3$ group by a ($d-d$) π -back-bonding process (163). [A similar suggestion has been made for an Sn—Mn system (153)]. An order of increasing $-\text{SiMe}_3$ shift in $\text{Me}_3\text{SiFeL}_2\text{Cp}$ may be correlated (163) with decreasing π -acceptor capacity of the ligands L_2 :



The magnitude of $\mathcal{J}(\text{Pt}-\text{P})$ for some phosphine-substituted SiPt complexes depends on the covalency of the Pt—P bond (136). Such a bond is relatively ionic in a system where it lies trans to a ligand of high trans influence and $\mathcal{J}(\text{Pt}-\text{P})$ is then small. The coupling in cis complexes decreased in the order $\text{Cl} \gg \text{C} > \text{Si}$ and since a comparable situation has been observed for methyl-Pt compounds it is suggested that the effect is one of σ - rather than π -interaction.

4. Mass Spectrometric Studies

As with NMR spectroscopy, the use of mass spectra has become a standard method of characterizing new transition metal complexes (42, 59, 226). Most of the fragmentation data for transition metal silyls are for simple carbonyls. The compounds $\text{X}_3\text{SiM}(\text{CO})_n$ [$\text{M} = \text{Mn}, \text{Re}, n = 5, \text{X} = \text{F}, \text{C}_6\text{F}_5$; $\text{M} = \text{Co}, n = 4, \text{X}_3 = \text{F}_3, (\text{C}_6\text{F}_5)_3, \text{MeF}_2$] all exhibit reasonably intense molecular ions and show successive loss of CO to give X_3SiM^+ as a major fragment ion (210, 211, 217, 218). The spectrum of $\text{H}_3\text{SiCo}(\text{CO})_4$ was similar, but contained only a very weak molecular ion (9), while with $\text{H}_3\text{SiMn}(\text{CO})_5$ only $\text{H}_3\text{SiMn}(\text{CO})_4^+$ and lower derivatives were observed, H_3SiMn^+ being absent (10). With one exception, this loss of CO from the transition metal was a more favorable reaction pathway than loss of X from silicon. An alternative initial breakdown, loss of $[\text{C}_6\text{F}_5]$, was observed in the spectrum of $(\text{C}_6\text{F}_5)_3\text{SiRe}(\text{CO})_5$ (217); CO ligands were, however, lost subsequently. Degradation of the $(\text{C}_6\text{F}_5)_3\text{Si}^+$ ion followed previously observed routes. The base peak in most cases was that of the metal ion M^+ . Ligand transfer, a frequent occurrence in metal-metal bonded compounds

(59), from Si to M was observed in the form of rearranged ions [e.g., $\text{FM}(\text{CO})^+$ and FM^+]: These processes appear to involve elimination of $:\text{SiF}_2$ and it has been suggested that an XF_2SiM derivative ($\text{X} = \text{F}, \text{Me}$) might be a suitable precursor at low temperatures (210). The ready loss of Me from Me_3Si derivatives is as well established as the loss of CO from metal carbonyls, and in the compound $\text{Me}_3\text{Si}(\text{Me}_2\text{Si})\text{Fe}(\text{CO})_2\text{Cp}$ both reactions were observed (164). In the series $\text{H}_3\text{SiM}(\text{CO})_3\text{Cp}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$), fragmentation occurred by loss of $-\text{SiH}_3$ and carbonyl groups although the Mo derivative was exceptional in giving no ions containing the $-\text{SiH}_3$ function (124).

The cracking patterns of the complexes $\text{Cl}_3\text{M}'\text{Ru}(\text{CO})_2\text{Cp}$ ($\text{M}' = \text{Si}, \text{Sn}$) have been compared (35). The Si compound lost 2CO and then 3Cl stepwise, but the base peak was $[\text{Cl}_3\text{SiRuCp}]^+$. Ligand transfer gave rise to CpM'^+ ions. In neither spectrum was $\text{M}'\text{Ru}^+$ found, indicating that the $\text{Cp}-\text{Ru}$ link is stronger than either $\text{Ru}-\text{M}'$ or $\text{Ru}-\text{CO}$.

The mass spectrum of $[\text{Cl}_3\text{SiRu}(\text{CO})_4]_2$ showed a parent ion for the dimer and stepwise loss of 8CO units. The ion $\text{Cl}_3\text{SiRu}(\text{CO})_4^+$ was also observed, but its intensity was lower than that of the corresponding ion from the $\text{Me}_3\text{Si}-$ analog, indicating a stronger $\text{Ru}-\text{Ru}$ bond when $\text{Cl}_3\text{Si}-$ rather than $\text{Me}_3\text{Si}-$ was a ligand (169). Negative ion spectra of some Co and Mn derivatives have been reported (213).

Studies of appearance potentials have given data on $\text{Si}-\text{M}$ bond dissociation energies (210–212). Values for $D(\text{Si}-\text{Co})$ in $\text{MeF}_2\text{SiCo}(\text{CO})_4$ (127 ± 15) and $\text{F}_3\text{SiCo}(\text{CO})_4$ ($105 \pm 12 \text{ kcal mole}^{-1}$) were proposed, but these are probably much too high in the light of studies on $\text{Me}_3\text{M}'\text{M}(\text{CO})_3\text{Cp}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{M}' = \text{Ge}, \text{Sn}$) (49).

5. Miscellaneous Studies

Electric dipole moment measurements on $\text{R}_3\text{SiCo}(\text{CO})_4$, $(\text{R}_3\text{Si})_2\text{Fe}(\text{CO})_4$, and related compounds have indicated a relationship between $\nu(\text{CO})$ and charge transfer in the $\text{Si}-\text{M}$ bond within a given series: the central transition metal is apparently not charged (156). Application of the relationship to $\text{H}_3\text{SiCo}(\text{CO})_4$ suggests a small bond dipole in the sense



The dipole moment (2.5 D) of $\text{Ph}_2\text{MeSiPtCl}(\text{PMe}_2\text{Ph})_2$ is consistent with the trans configuration (63).

Absorption ($33\text{--}55,000 \text{ cm}^{-1}$) spectra and laser Raman spectra, as well as

vibrational analyses, have been reported for the series $\text{Cl}_3\text{MCo}(\text{CO})_4$ ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}$) (235). Ligand exchange processes in $(\text{Cl}_3\text{Si})_2\text{Ru}(\text{CO})_4$ and $(\text{Me}_3\text{Si})_2\text{Os}(\text{CO})_4$ have been investigated using IR and NMR spectroscopy (203a, 203b). The compounds $\text{LCo}(\text{CO})_4$ ($\text{L} = \text{Me}_3\text{Si}, \text{Ph}_3\text{Si}, \text{Cl}_3\text{Si}, \text{R}_3\text{Sn}, \text{R}_3\text{Ge}, \text{and } \text{R}_3\text{Pb}$) and $\text{Cl}_3\text{SiCo}(\text{CO})_3(n\text{-Bu}_3\text{P})$ have been studied by IR, NMR (196a, 227), and NQR (41, 196a, 227) techniques. The Mössbauer spectra of *cis*-(H_3Si) $_2\text{Fe}(\text{CO})_4$ and *cis*-(H_3Si) $\text{HFe}(\text{CO})_4$ have been examined (5, 21). Polarograms have been recorded for $[(\text{Cl}_3\text{Si})_2\text{Fe}(\text{CO})\text{Cp}]^-$ and $\text{Cl}_3\text{SiFe}(\text{CO})_2\text{Cp}$ before and after coulometric reduction (36).

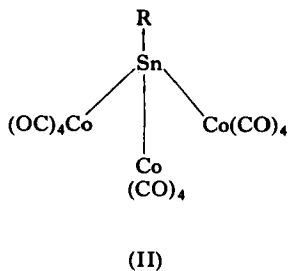
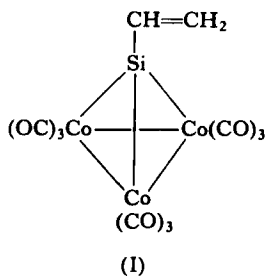
Structural data from X-ray- and electron-diffraction studies, mass spectra, and MO calculations were analyzed for $\text{R}_3\text{SiCo}(\text{CO})_4$ ($\text{R} = \text{H}, \text{F}, \text{Cl}$) and $\text{Me}_3\text{SiMn}(\text{CO})_5$; it was believed that there is partial double-bond character between Si and Co and that there may be intramolecular interaction between the axial silicon atom and the equatorial carbonyl groups (30, 212).

E. Silicon-Transition Metal Complexes Having Special Structural Features

These complexes are listed in Table IV. An attempt is made to provide some classification and rationalization, but many of the compounds have so far received only brief mention in the literature and some of the structures shown are not substantiated.

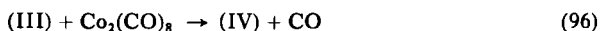
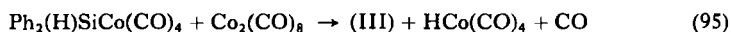
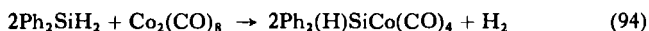
1. Polynuclear Cobalt Compounds

The reaction between $\text{Co}_2(\text{CO})_8$ and tetravinylsilane was reported to afford $(\text{CH}_2=\text{CH})\text{SiCo}_3(\text{CO})_9$ (161). This was thought to be the Si analog (I) of the $\text{RCCo}_3(\text{CO})_9$ series; members of this series are known to be tetrahedral with Co—Co bonds (102, 172, 186). The higher $\nu(\text{CO})$ for (I)

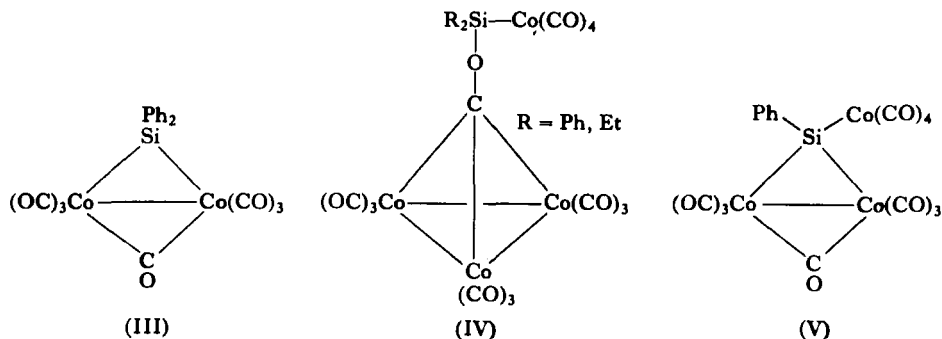


than for the C compounds was taken to indicate a measure of Si—Co (*d-d*) π -bonding. A second compound $[\text{SiCo}_3(\text{CO})_9]_2$ prepared by reaction of $\text{Co}_2(\text{CO})_8$ with Ph_4Si , was thought to contain two $[-\text{SiCo}_3(\text{CO})_9]$ units, as in (I), linked by an Si—Si bond, as in the corresponding cobalt carbonyl carbide (162). These structures were subsequently criticized when the organotin derivatives $\text{R}_2\text{Sn}[\text{Co}(\text{CO})_4]_3$ ($\text{R} = \text{CH}_3$, *n*- C_4H_9 , $\text{CH}_2=\text{CH}$, Ph, Cl, Br, I) (II) were characterized (146, 202).

There have been a number of reports concerning the reaction of $\text{Co}_2(\text{CO})_8$ with Ph_2SiH_2 . Originally, $\text{Ph}_2(\text{H})\text{SiCo}(\text{CO})_4$ was the only product isolated (57). More recently, $\text{Ph}_2\text{SiCo}_2(\text{CO})_7$ (III) (18) and $\text{Ph}_2\text{SiCo}_4(\text{CO})_{14}$ (IV) (110) have been identified and the diethyl analog of (IV) was prepared similarly (110). From an IR study of the $\text{Ph}_2\text{SiH}_2/\text{Co}_2(\text{CO})_8$ reaction, the sequence of Eqs. (94)–(96) was suggested (110).



The reaction of $\text{Co}_2(\text{CO})_8$ with PhSiH_3 has given $\text{PhSiCo}_3(\text{CO})_{11}$ (V) (18). Structures (III)–(V) are tentatively proposed, (III) and (V) by analogy with those established for the corresponding Ge compounds. When heated, (V) decomposed; formation of $\text{PhSiCo}_3(\text{CO})_9$ was not detected (18) (see Section II,E,6).

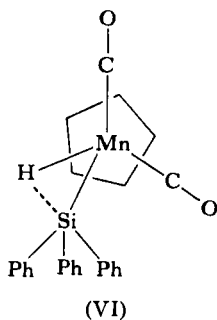


2. Complexes with Hydrogen-Bridged Silicon–Transition Metal Bonds

In 1969, Hoyano, Elder, and Graham reported the synthesis of the complexes $\text{Ph}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$, $\text{Ph}_2\text{SiD}_2\text{Re}_2(\text{CO})_8$, and $\text{Me}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$ (143). Spectroscopic evidence strongly suggested that these compounds are

transition metal hydrides of a new type with hydrogen atoms bridging the Si—Re bonds. A single-crystal X-ray diffraction study on $\text{Ph}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$ failed to locate the bridging hydrogen atoms, but indicated that a hydrogen occupies the otherwise vacant sixth coordination site of each of the two rhenium atoms, forming bridges to the silicon. Further members (26) of this class are shown in Table IV. All the compounds are produced by UV irradiation of the parent silanes with the appropriate metal carbonyls.

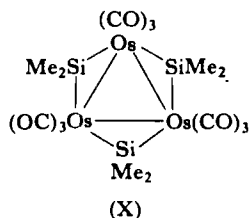
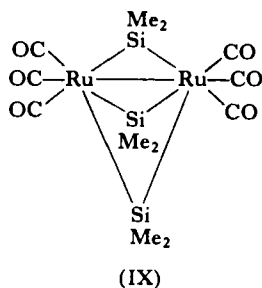
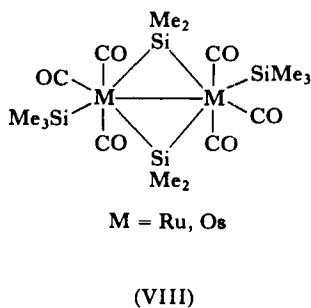
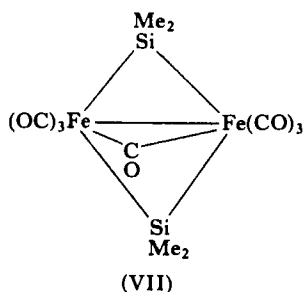
An X-ray study of the Mn derivative (VI) has located the single bridging hydrogen atom (26). The Si—H bond length is 1.76 Å, compared with a normal length of 1.48 Å, and the sum of the van der Waals radii, 3.1 Å. The bridging hydrogen atom is 2.07 Å away from the carbon atom of the adjacent carbonyl group.



A recent X-ray study of $(\text{Et}_2\text{Si})_2\text{H}_2\text{W}_2(\text{CO})_8$ has been interpreted in terms of two W—Si bonds [2.586(5) Å] and two 3-center 2-electron W—H—Si bonds [2.703(4) Å] (26a).

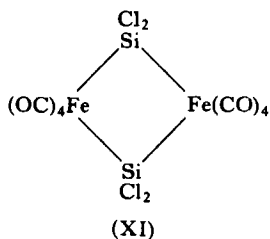
3. Silylene Complexes and Compounds with $\text{R}_2\text{Si} \leftarrow$ Bridges

The reaction between $\text{HMe}_2\text{Si}—\text{SiMe}_2\text{H}$ and $\text{Fe}(\text{CO})_5$ in cyclohexane, either photochemically at 30°C or thermally at 120°C, has given $(\text{Me}_2\text{Si})_2\text{Fe}_2(\text{CO})_7$, (VII) (174). Related compounds, involving GePh_2 (107) and GeMe_2 (3) bridges, are known. An X-ray study has established the structural type (VII) for $(\text{Ph}_2\text{Ge})_2\text{Fe}_2(\text{CO})_7$, (107). The Me_2Si bridges of (VII) show fluxional behavior (activation energy, 9 kcal mole⁻¹): the ¹H NMR spectrum at -72°C consists of two resonances which coalesce at -46.5°C (90 MHz) to give a broad signal sharpening to a singlet at 25°C

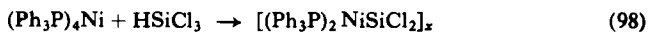
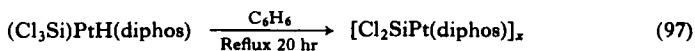


(8.89 τ). Reactions between disilanes ($\text{Me}_3\text{SiSiMe}_2\text{H}$, $\text{HMe}_2\text{SiSiMe}_2\text{H}$) and Ru and Os carbonyl complexes have afforded (VIII)–(X) (39).

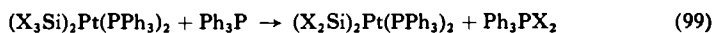
The compound $[\text{Cl}_2\text{SiFe}(\text{CO})_4]_2$ is obtained from $\text{Fe}(\text{CO})_5$ and HSiCl_3 , in a sealed tube reaction (148). It is presumably a member of the family of Group IVB–iron metallocycles of structural type (XI) (40, 246). Two Ni



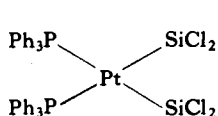
group derivatives, possibly also of this type, have been obtained [Eqs. (97) (65), (98) (177)]. However, if the products of Eqs. (97) and (98) were mono-



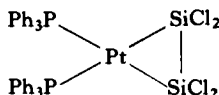
meric they could then be formulated as complexes containing the dichlorosilylene ligand. Such a formulation has been proposed for two platinum compounds [Eq. (99) ($\text{X} = \text{Cl}, \text{Br}$) (215)].



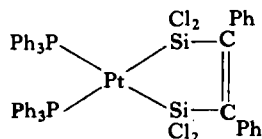
The complex $(\text{Ph}_3\text{P})_2\text{Pt}(\text{SiCl}_2)_2$ was monomeric in benzene, and reacted with diphenylacetylene to give a 1:1 adduct (also monomeric in benzene). On this basis, together with IR data, structure (XII) rather than (XIII) was preferred for the SiX_2 compounds, and the adduct was formulated as (XIV).



(XII)



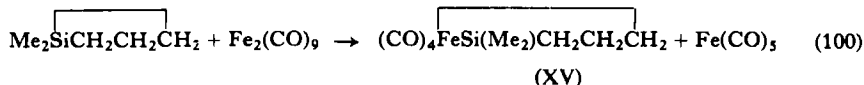
(XIII)



(XIV)

4. Derivatives of Strained Organosilicon Heterocycles

The strained-ring compound 1,1-dimethyl-1-silacyclobutane (which may be regarded as an "olefin" of organosilicon chemistry) reacts with diiron nonacarbonyl in benzene at $6^\circ\text{--}20^\circ\text{C}$ as shown in Eq. (100) (89). (There is here some analogy with the reactions of transition metal complexes with strained hydrocarbons, which often produce valence tautomerization.) The



proposed structure for (XV), together with some representative reactions, is shown in Fig. 4. Compound (XV), which is thermally stable, is unusual in having both Si—M and C—M bonds and may be the forerunner of a family of stable transition metal chelate alkyls. The insertion of an $[\text{Fe}(\text{CO})_4]$ unit

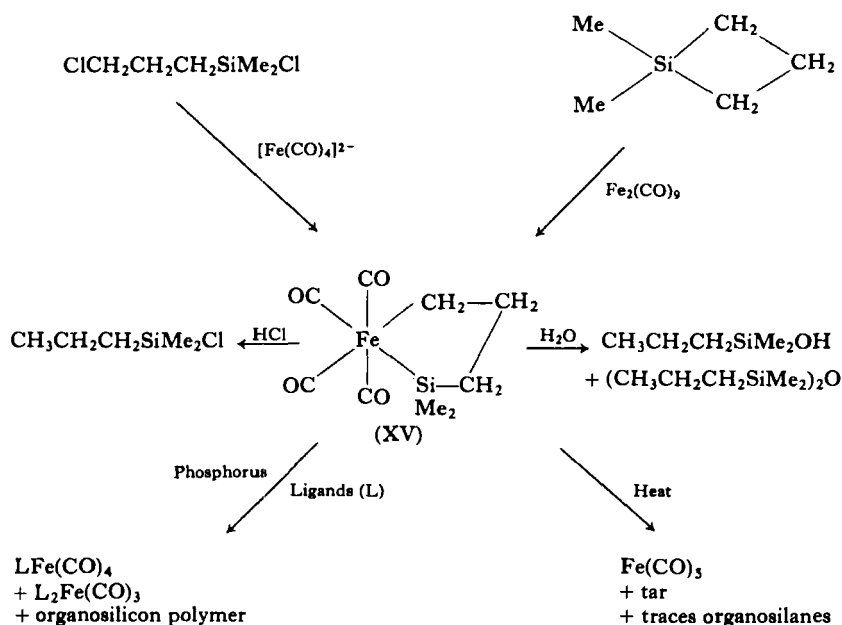
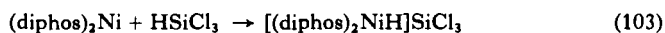
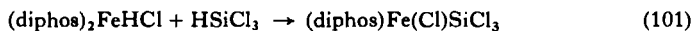


FIG. 4. Synthesis and reactions of a ferrasilacyclopentane.

under these conditions appears to be a general reaction for silacyclobutanes, 1,3-disilacyclobutanes, and 2,3-benzo-1-silacyclobutenes. Complexes of type (XV) may play a role in the transition metal-catalyzed [e.g., using $(\text{Ph}_3\text{P})_3\text{RhX}$ ($\text{X} = \text{Cl}, \text{CH}_3$)] polymerization of such strained silicon heterocycles, as illustrated for a silacyclobutane in Fig. 5 ($\text{L}_x\text{M}-\text{X}$ represents the transition metal complex) (88).

5. Compounds with $[\text{SiX}_3]^-$ and Related Anions²

The reactions of silicon hydrides with low-valent phosphine complexes of Fe, Co, and Ni have led to the isolation of a number of products in some of which the silicon moiety may be present as an $[\text{SiX}_3]^-$ anion (177). Examples are given in Eqs. (102)–(103).² Definitive confirmation of these formulations



² A complication in these reactions is that HCl gas reacts with the low oxidation state, e.g., $\text{Co}(\text{I})$, substrates, and HCl are difficult to remove from chlorosilanes (248).

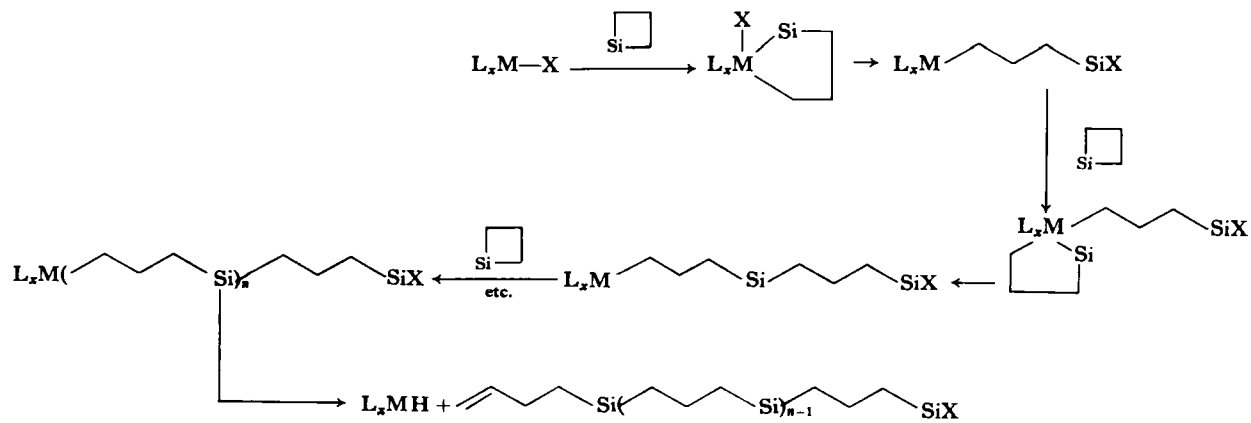
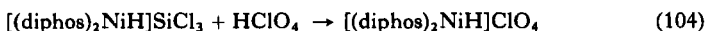


FIG. 5. Mechanism of the transition metal-catalyzed polymerization of a silacyclobutane.

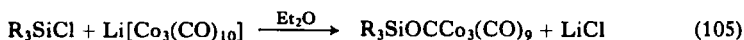
is not available. However, IR spectra serve to identify the *cations* of Eqs. (101)–(103), which are also known as the perchlorates. The latter may be obtained as in Eq. (104) (177).



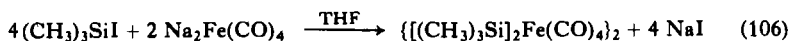
These compounds form an interesting contrast to the Lewis base adducts of silyl-metal carbonyls (Section II,C,4), where silicon is thought to be present in a cation.

6. ($R_3\text{Si}-\text{O}-$)-Bonded Derivatives of Transition Metal Carbonyls

It has been noted (Section II,B,1) that reactions between transition metal carbonyl anions and silicon halides often fail to produce species containing silicon–transition metal bonds, and that such failure has been ascribed to nucleophilic attack by carbonyl oxygen. It is therefore interesting that compounds containing $\text{Si}-\text{O}-\text{C}$ –transition metal linkages have recently been isolated from such reactions [Eqs. (105) ($R = \text{Me}, \text{Ph}$) (183) and (106)

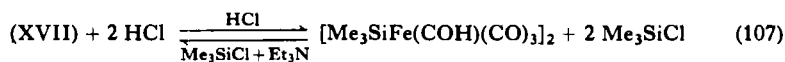


(XVI)



(XVII)

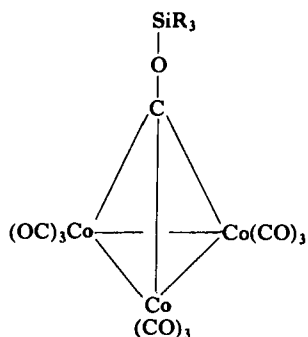
(192, 192a)]. The dimeric complex (XVII) appears to react with anhydrous



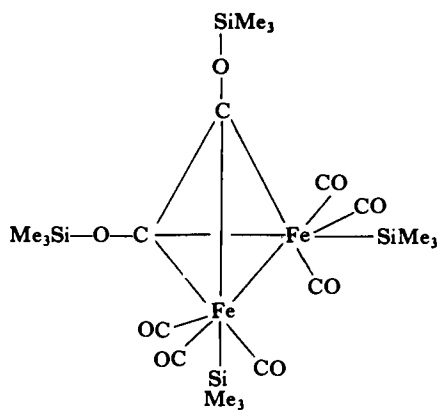
(XVIII)

HCl as in Eq. (107). The structures proposed for (XVI)–(XVIII) are shown below; a single crystal X-ray study of (XVII) is in progress (192, 192a).

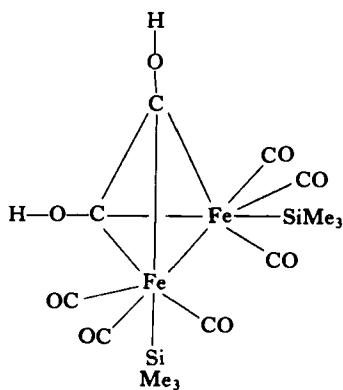
The complexes $R_2\text{SiCo}_4(\text{CO})_{14}$ ($R = \text{Et}, \text{Ph}$) also contain a $\text{Si}-\text{O}-\text{C}-\text{Co}$ linkage (Section II,E,1).



(XVI) R = Me, Ph



(XVII)



(XVIII)

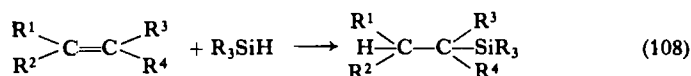
Note: It is now known (247) that structures (XVII) and (XVIII) are incorrect, and that (XVII), correctly formulated (Me₃SiOC)₄Fe₂(CO)₆, contains a ferracyclopentadiene skeleton.

III

TRANSITION METAL-CATALYZED HOMOGENEOUS HYDROSILYLATION

A. Introduction

Substantial advances have been made in the field of hydrosilylation [Eq. (108)] since 1965, when a comprehensive mechanism (Fig. 6) for catalysis by



noble metal complexes was first published (55). Section III covers this era and is specific to homogeneous hydrosilylation with particular emphasis on the organo(transition)metallic catalyst involved. [A summary of the General Electric Company contribution to this field is available (54)]. Excluded, therefore, are other catalytic systems (metals on supports, radical initiators, organic bases, UV irradiation, etc.), all of which have been largely superseded by the new transition metal systems, and which, in any case, are well documented (105, 180). The nature of the reacting substrates (olefin and silane) will not be discussed in detail except where this is of direct relevance to the *inorganic* standpoint.

Hydrosilylation and related reactions of silanes are now of industrial significance (196). The reaction was first observed at high temperature as early as 1945, but the major credit for its discovery rests with Sommer and co-workers who, in 1947, obtained a quantitative addition reaction between 1-octene and HSiCl_3 in the presence of diacetyl peroxide (225). Hydrosilylation is an extremely useful tool for attaching organic fragments containing reactive functional groups to Si and for the cross-linking of silicone polymers. This finds application in the intermediates, resins, and rubbers technology of silicones (105, 196). Its importance in the latter area must surely grow as the nature of homogeneous catalysis becomes better understood and tailor-made products (e.g., a material inert at ambient temperature but heat-activated) are developed for an increasingly sophisticated market. Silicone RTV (room-temperature-vulcanized) rubbers based on this reaction are superior to others in the silicone field, in that they exhibit excellent storage and heat stability together with rapid heat cure, low shrinkage, and the absence of volatile by-products. The one major disadvantage of transition metal catalyst systems is their susceptibility to poisoning, particularly by good donors.

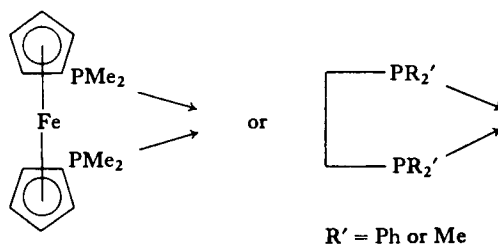
The most common catalyst used to date is chloroplatinic acid (also known, after its discoverer, as Speier's catalyst); it is now clear that, contrary to earlier views (23), hydrosilylation is a homogeneous process (25, 208). A major problem is that of reproducibility, and efforts are being made to utilize soluble transition metal complexes. Information about such systems has been used in the interpretation of some related catalytic heterogeneous reactions (232).

The types of transition metal complexes used in hydrosilylation are shown

TABLE VI
SOME HYDROSILYLATION COMPLEXES OF GROUP VIII

Complex ^a	References
Co ₂ (CO) ₈	13, 52, 57, 130
HCo(CO) ₄	13, 14, 57
(Ph ₃ P) ₃ Co(H)X	5
(Ph ₃ P) ₃ RhCl	52, 60, 135
(R ₃ P) ₂ Rh(CO)Cl	60, 135
(Ph ₃ P) ₃ Rh(CO)H	52
Rh ₂ Cl ₂ Y ₄	52, 55, 60
Cl ₂ EtSiRhHCl(PPh ₃) ₂	135
(chelate)NiCl ₂	173
(Ph ₃ P) ₂ PdZ	229
(Ph ₃ P) ₄ Pd	128, 229
(Ph ₃ P) ₄ Pt	229
Pt ₂ Cl ₄ (olefin) ₂	25, 55, 204, 224
(Ph ₃ P) ₂ Pt(C ₂ H ₄)	240
Ziegler-type catalysts [e.g., Co(acac) ₃ /AlEt ₃]	178

^a R = Ph or Et; X = H₂, N₂, or (H)Si(OEt)₃; Y = CO or C₂H₄; Z = maleic anhydride or *p*-benzoquinone; olefin = ethylene, ethylcyclohexene, styrene, etc.; acac = acetylacetonato; (chelate) =



in Table VI; no attempt has been made to cover the extensive patent literature. Though salts or complexes of numerous elements have been claimed as catalysts, the vast majority of published work concerns Group VIII systems (105, 180); no active osmium complexes have been reported and this may be associated with their high cost. Iron carbonyls have been used by Russian workers, but high temperatures (130–140°C) are required (e.g., 175a). Early reports suggested that soluble Pd(II) complexes do not catalyze hydrosilylation because of their ease of reduction (55), but later work (128, 229) serves to emphasize that a noble metal provides a suitable center for homogeneous catalysis given a suitable coordination environment.

The initial reaction (1), which probably occurs during the induction period commonly accompanying hydrosilylations, is the silane reduction of the catalyst, a d^6 Pt(IV) complex. The resulting square-planar d^8 Pt(II) complex (XIX), which either contains a weakly held ligand or solvent molecule capable of ready replacement within its coordination sphere, then (step 2) coordinates, and hence activates, substrate olefin. The importance of vacant sites within the coordination sphere of a homogeneous catalyst molecule has often been emphasized (78*a*, 79), and coordinated olefins are known to show enhanced susceptibility to attack by nucleophiles (129); this might include H^- derived from Si—H cleavage (55). A complex such as (XX) is clearly related to Zeise's anion (87). It is noteworthy that the latter, as well as other olefin Pt(II) and Rh(I) complexes are catalysts (55); their activity in terms of the scheme of Fig. 6 requires an olefin-olefin exchange step at the transition metal center and this is a well-known process.

In step (3), silane adds oxidatively (see Section II,B,7) to provide a d^6 octahedral intermediate (XXI). The d^8 and d^{10} complexes of Table VI are such that they readily undergo oxidative addition (79, 133), including hydrosilylation (Section II,B,7). Often, for d^8 substrates, oxidative additions occur most readily with third-row elements and those on the left of Group VIII [i.e., Os(0) the most reactive and Ni(II) the least (79)]. Reversibility in these systems is well established [e.g., $Ir(I) \rightleftharpoons Ir(III)$ (233)] and has specifically been noted for silanes (51, 55, 132, 133) (Section II,B,7). The catalysis by chloroplatinic acid of H/D exchange at silicon may be accounted for by a similar mechanism (203). This reaction proceeds with retention of configuration at Si and it is therefore probable that retention also occurs in step (3), because the overall hydrosilylation process likewise occurs with retention (224). Retention of configuration at Si in transition metal-catalyzed hydrosilylation, and evidence that silanes add in a *cis* manner (23, 219), has the following mechanistic implications: (a) step (4) must involve *cis* addition of hydrogen and platinum to the double bond, and (b) the formation of the hydrosilylated product (XXIII) occurs with retention of configuration at both Si and C (224). Consistent with this, when the unsaturated substrate is $RC\equiv CH$ or 1-methyl- d_3 -cyclohexene, stereo-specific *cis* addition results in the formation of the *trans*-hydrosilylated product (XXIII) (23, 219).

Step (4) has recently been suggested to be rate-determining (204); it involves a rearrangement from an olefin π - to an alkyl σ -complex. The latter is postulated to react with more olefin [step (5)], regenerating (XX) and

forming the hydrosilylated product (XXIII); the cycle is thus complete. Step (4) must be assumed to be reversible in order to account for the isomerization of the olefin which frequently accompanies hydrosilylation (105). Stepwise isomerization along an alkyl chain may alternatively (Fig. 7) be explained by the involvement of π -allyl-hydrido-metal species.

The mechanism for hydrosilylation in Figs. 6 and 7 clearly has much in common with suggestions regarding homogeneous transition metal catalysis for other processes involving olefins, such as hydrogenation, isomerization, the oxo reaction, and oligo- and polymerization.

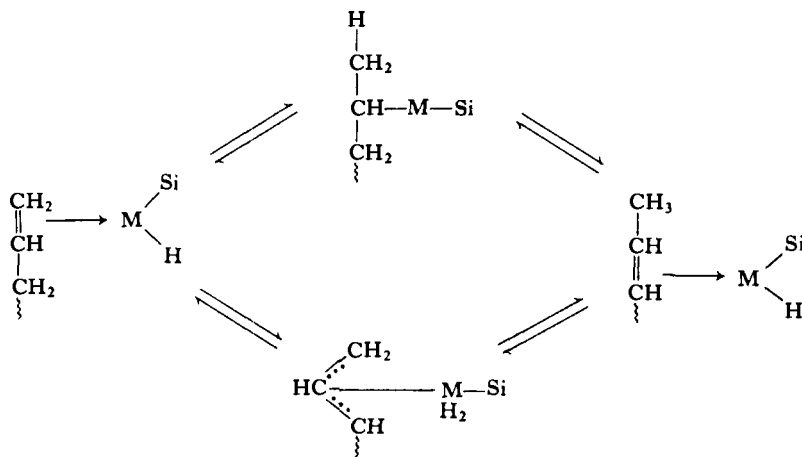
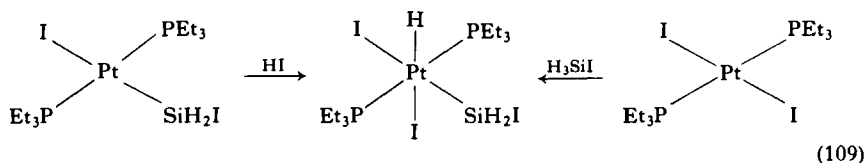


FIG. 7. Isomerization and hydrosilylation.

C. Other Transition Metal Systems as Models for the Hydrosilylation Mechanism

The chloroplatinic acid system is not suitable for the identification of intermediates, such as those suggested in Fig. 6. However, related complexes have been obtained, or evidence for their formation has been provided, in other systems, which we may therefore regard as models. Reference is also made to Sections II,B,4 and 7, and II,C,3.

A six-coordinate Pt(IV) compound [Eq. (109)] has recently been characterized (27, 29) (see Sections II,B,7 and II,C,3a); this has both Pt—Si and Pt—H but not Pt—olefin, [such as (XXI)] or Pt—alkyl [such as (XXII)] bonds.



Si—Pt(IV) complexes have been suggested as intermediates in other reactions involving Pt(II) reagents: e.g., *trans*-R₃SiPtCl(PEt₃)₂ + GeH₃Cl (28), HCl (71), H₂ (71), and PhC≡CH (114); *trans*-(Et₃P)₂Pt(D)Cl + SiH₃Cl (27); and *cis*-(Bu₃P)₂PtCl₂ + R₃SiH (54). Similarly, synthetic routes to Si—M compounds have sometimes been considered to proceed via such species (71) (Section II,B,4 and 5).

The *d*⁸ Ir(I) complexes *trans*-(Ph₃P)₂Ir(CO)Cl and (Ph₃P)₃Ir(CO)H have been studied as hydrosilylation models (51, 54, 55, 131, 132). They are *not* hydrosilylation catalysts though both oxidatively add silanes and the addition is reversible (Fig. 8 and Section II,B,7). The ambient temperature

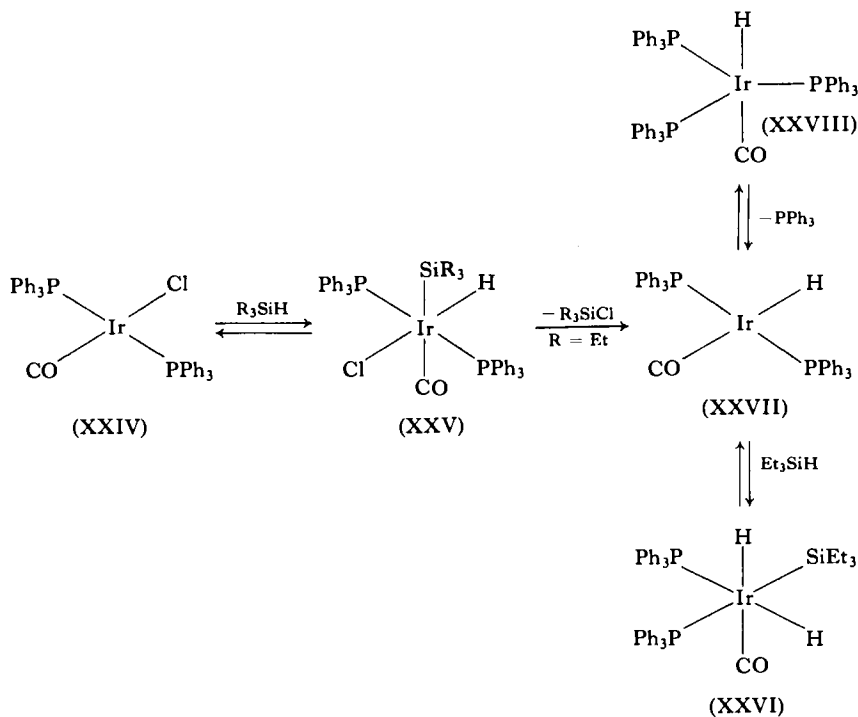
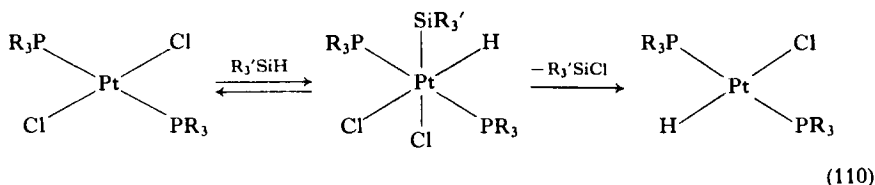


FIG. 8. An iridium hydrosilylation model system.

equilibrium (XXIV) \rightleftharpoons (XXV) is markedly dependent on the electronegativity of the groups attached to Si; only when these are strongly electronegative (e.g., Cl) is (XXV) isolated (54, 55). Such results have recently been given a quantitative description based on differences in the activation enthalpy of the reductive elimination process; the dominant factor governing the equilibrium is the strength of the Ir—Si bond and this decreases with increasing alkyl substitution at silicon (133).

For trialkylsilanes as substrates, evidence for the intermediacy of compounds (XXV) is available. Thus, *trans*-(Ph₃P)₂Ir(CO)Cl is an efficient catalyst for H/D exchange at Si (223), and adds trialkylgermanes irreversibly (114). It is probable, therefore, that for R₃SiH the equilibrium is almost wholly in favor of (XXIV). The latter reacts with Et₃SiH at reflux to give the silyldihydrido complex (XXVI) (51). The chlorotrialkylsilane elimination step and the interrelation of (XXIV), (XXV), and (XXVII) is similar to that suggested for the Cl/H exchange of Eq. (110) (54, 55).



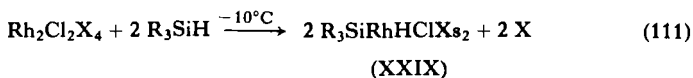
Complex (XXVI) may also be obtained from (XXVIII) (51, 131, 132), with (XXVII) (132) as intermediate. Confirmation for the two equilibria was provided when it was demonstrated that by varying the concentrations of Et₃SiH and Ph₃P the ratio of (XXVI):(XXVIII) was altered (54). The stereochemistry shown for (XXVI) has not been confirmed, but *cis* addition to (XXVII) is likely by analogy with the addition of hydrogen to *trans*-(Ph₃P)₂Ir(CO)Cl and of silanes to (Ph₃P)₃Ir(CO)H (131). The greater stability of complexes (XXVI) than their chloro analogs (XXV) is in accord with the view that oxidative additions are promoted by electron-releasing ligands within the coordination sphere of the reactant complex (79).

The hydrosilylation inactivity of *trans*-(Ph₃P)₂Ir(CO)Cl may be due to the strength of the P—I bonds. Thus, the Rh(I) analog is an active catalyst (52, 60, 135) and indeed is superior to the hydrogenation catalyst (Ph₃P)₃RhCl (197). Oxidative addition of silanes to both Rh complexes is well known (Section II,B,7) (132) and the adducts are believed to have a trigonal bipyramidal configuration, as has been confirmed in one case by an

X-ray diffraction study (173). Attempts to obtain a six-coordinate species by addition of excess ligand (MePh_2P , C_2H_4 , or CO) usually results in silane elimination (Section II,C,3f) (60, 132).

The complex $\text{Cl}_3\text{SiRhHCl}(\text{PPh}_3)_2$, in which a potentially free sixth coordination site about the Rh atom is blocked by a phenyl hydrogen atom (191), has low activity. Olefin does not insert into the Rh—H bond (54, 60), and hence this complex is not likely to be an intermediate in the hydrosilylation of olefins using $(\text{Ph}_3\text{P})_3\text{RhCl}$. Factors influencing the relative importance of ligand replacement and olefin π - to alkyl σ -metal bonding have been discussed (54).

Of the Rh complexes so far examined, the chlorine-bridged $\text{Rh}_2\text{Cl}_2\text{X}_4$ ($\text{X} = \text{CO}$ or C_2H_4) are the most efficient, causing exothermic reaction of 1-hexene and R_3SiH at ambient temperature (55, 60). The active catalyst is believed to be (XXIX) [Eq. (111) ($\text{X} = \text{CO}$, C_2H_4 ; $s = \text{solvent}$) (60)]. A reactivity order ($\text{R} = \text{Et}$ or Ph) based on yields is $\text{Rh}_2\text{Cl}_2\text{X}_4 > (\text{R}_3\text{P})_2\text{Rh}(\text{CO})\text{Cl} > (\text{Ph}_3\text{P})_3\text{RhCl}$, but the positions of the last two appear to be reversed at 60°C (135). Adventitious traces of oxygen have a marked



catalytic effect (60). The complex $(\text{Ph}_3\text{P})_3\text{RhCl}$ with HSiCl_3 is not particularly efficient at 15°C (60), but is a satisfactory hydrosilylation catalyst when used in a closed system at higher temperature (135). The yield of the hydrosilylated product $\text{C}_6\text{H}_{13}\text{SiR}_3$ ($\text{R} = \text{Ph} > \text{Et} > \text{Cl}$) is inversely proportional to the stability of the complexes $\text{R}_3\text{SiRhH}(\text{Cl})(\text{PPh}_3)_2$ (135). Excess of 1-hexene is not isomerized during the reaction and the hexylsilanes formed are essentially terminal. This complex is interesting in that, unlike other common catalysts, including H_2PtCl_6 , the rate of hydrosilylation is greater than that of isomerization (52). An analogous situation has been reported for hydrogenation but both hydrogen atoms were believed to add to the olefin in a concerted fashion (197). A similar scheme for hydrosilylation would not allow for isomerization, yet internal olefins (e.g., 2-pentene) yield terminal products (52, 135).

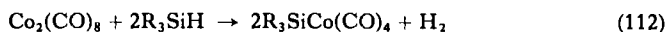
The complex $\text{EtCl}_2\text{SiRhH}(\text{Cl})(\text{PPh}_3)_2$, unlike the Cl_3Si analog, has identical activity to $(\text{Ph}_3\text{P})_3\text{RhCl}$. It has been suggested that both compounds predissociate to afford the same active species (135).

An interesting study has been made of the susceptibility of rhodium catalysts to inhibitors (52). Good yields of adduct are obtained from the

reaction of PhMe_2SiH with acrylonitrile, using $(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})\text{H}$; in this system, there presumably is free phosphine. Triphenylphosphine and acrylonitrile are frequently used to inhibit olefin hydrosilylations catalyzed by platinum. The same Rh complex is also active in the presence of a tenfold excess of tributylamine. Such catalysts may therefore have a useful role for hydrosilylations of strongly coordinating olefins; the behavior of the Rh compound has been likened to the "poisoned" heterogeneous hydrogenation catalysts due to Lindlar (52). $(\text{Ph}_3\text{P})_4\text{Pt}$ also functions as a catalyst (229), and yet dissociates to give free phosphine (82).

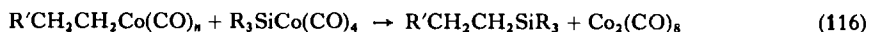
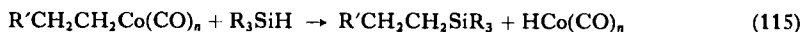
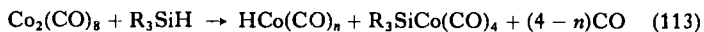
By analogy with hydroformylation, dicobalt octacarbonyl has been examined as a hydrosilylation catalyst. Various silanes and α -olefins react, often exothermically. Thermal deactivation occurs above 60°C ; hence, large exotherms and high temperatures must be avoided (56, 57, 130). Isomerization is more pronounced than for the bridged olefin complexes of Pt(II) and Rh(I) (see below); it even occurs with trialkoxysilanes (57). Though isomerization is faster than hydrosilylation, little variation in the *relative* rates of these two processes with the nature of the silane is observed; this is in marked contrast to the bridged systems (55).

Excess of the olefin is desirable so that the formation of Si—Co complexes [Eq. (112) and Section II,B,7] is suppressed (54, 57). These silyl complexes are not hydrosilylation catalysts.



When dicobalt octacarbonyl is added to the silane *prior* to olefin addition, the activity of the system is drastically reduced (13, 14).

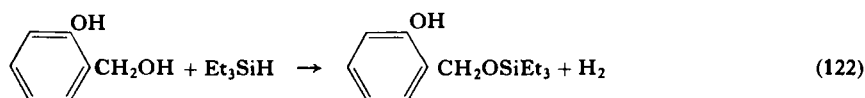
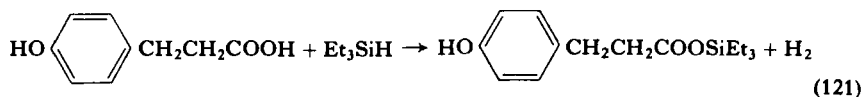
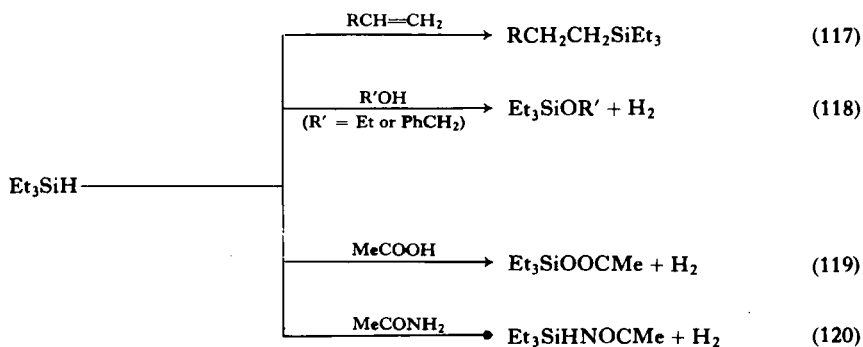
The proposed mechanism, due to Chalk and Harrod, is outlined in Eqs. (113)–(116) ($n = 3$ or 4), though it is recognized that this scheme is an oversimplification (54, 57); it is probable that, in the absence of CO pressure, the coordinatively unsaturated tricarbonyls, not tetracarbonyls, are the catalytic intermediate (54).



Consistent with this mechanism, $\text{HCo}(\text{CO})_4$ is an effective hydrosilylation catalyst (13, 14, 57). In the absence of olefin, $\text{R}_3\text{SiCo}(\text{CO})_4$ is formed (Section II,B,4).

Equation (114) is also a step in hydroformylation (54, 58) and has received independent confirmation. Equations (115) and (116) have not been tested, probably because of the ready CO insertion of alkylcobalt carbonyls (138). Reaction of alkylcobalt carbonyls, prepared *in situ*, with trialkylsilanes (giving tetraalkylsilanes) and with silylcobalt carbonyls (no alkyl substitution at silicon was observed) shows that Eq. (116) remains unproven (54). The intermediacy of an alkylcobalt species has been questioned, because hydrosilylation does not occur when the reactants [Me_3SiH , C_2H_4 , and $\text{HCo}(\text{CO})_4$] are mixed in the gaseous phase. This contrasts with the liquid-phase situation, where rapid reaction gives high yield of the hydrosilylated product. An alternative, highly polar intermediate was suggested, possibly a transitory π -olefin $\text{HCo}(\text{CO})_n$ complex, which might be stabilized by solvation (13, 14).

Two significant communications indicate the considerable potential of transition metal complexes as multifunctional homogeneous catalysts in the silane field (5, 53). Here the *same* catalyst activates silanes toward *different* substrates and it is probable that all proceed via a common metal hydrido intermediate. Both $\text{Co}_2(\text{CO})_8$ and $(\text{Ph}_3\text{P})_3\text{CoHX}$ [$\text{X} = \text{H}_2$, N_2 , or $(\text{H})\text{Si}(\text{OEt})_3$] catalyze *O*-silylation and hydrosilylation; the hydrogen on Si may be replaced by $\text{R}'\text{O}$, $\text{R}'\text{COO}$, $\text{R}'\text{CONH}$, or R_3SiO [e.g., Eqs. (117)–(120)], and excellent yields of silylated product result. Phenolic groups do



not undergo *O*-silylation, in what is an extremely selective reaction [Eqs. (121) and (122)] (53). The scope of such selective silylation in the protection of reactive organic groups has been stressed (53). Other reactions of silanes with transition metal complex catalysts which merit further study are halogenation and reaction with organic halides [including acyl halides (101)] (67, 104, 209), H/X exchange at silicon [X = halogen (104, 173), alkyl (22), deuterium (224)], the polymerization of strained ring species (e.g., silacyclobutane) (20, 88, 89, 182) (see Section II,E,4), Si—Si bond cleavage (240*a*), and the synthesis of organosilicon compounds by the Grignard route (84).

For catalysis by Pt(II) and Rh(I) π -olefin complexes (those containing chelating diolefin ligands were less effective), three types of reaction have been observed depending on the nature of the silane (55).

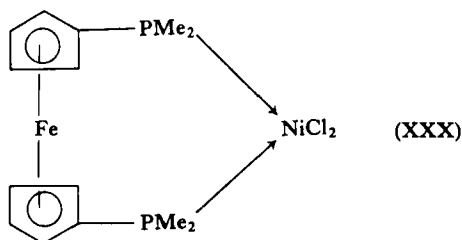
- (1) With alkoxysilanes, rapid hydrosilylation of the terminal olefin occurs, without isomerization, to give high yield of adduct.
- (2) The most common behavior, especially for substrates with Si—Cl bonds, is the extensive isomerization of excess of olefin during rapid hydrosilylation.
- (3) With alkyl- and arylsilanes, concurrent isomerization and hydrosilylation occur, but the rates of both processes fall away rapidly due to some reduction to the metal; such deactivation is temperature-dependent, and high yields of adduct are obtained with these silanes when additions are carried out slowly at ambient temperature.

Palladium complexes are readily reduced by silanes to the free metal, so that even with excess of olefin present they do not, in general, act as homogeneous catalysts in hydrosilylations (55). Recently, however, it has been shown that hydrosilylation of butadiene dimer occurs in the presence of bis(triphenylphosphine)palladium complexes containing maleic anhydride or benzoquinone ligands (229). R_3SiH ($R = Me$ or Et) gives the 1:2 adduct, $R_3SiCH_2CH=CHCH_2CH_2CH=CHCH_3$, exclusively, whereas Cl_3SiH and Me_2PhSiH afford normal 1:1 adducts $X_3SiCH_2CH=CH-CH_3$. Similar results were obtained using metallic palladium in the presence of excess of triphenylphosphine (128). It has been suggested that compounds containing Pd—H bonds are the active intermediates and that reaction proceeds by insertion of butadiene (223). A similar explanation for the formation of a significant quantity of $C_{12}H_{25}SiCl_3$, during the reaction of $HSiCl_3$ with 1-hexene catalyzed by $Rh_2Cl_2(CO)_4$, requires the consecutive

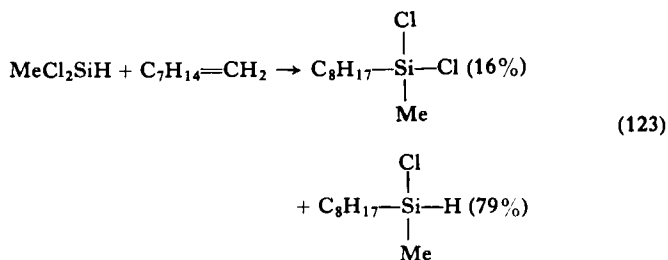
insertion of olefin into Rh—H and Rh—alkyl bonds (60). This 2 olefin:1 silane adduct is not observed when the more readily polymerizable C_2H_4 is the substrate (52). Interestingly, high molecular weight polymer has been obtained from tetrahydrofuran and other cyclic oxides in the presence of a $Co_2(CO)_8$ /silane mixture at ambient temperatures (53).

$(Ph_3P)_4Pd$ and certain Pd(II) complexes in the presence of an excess of a tertiary phosphine also function as active catalysts (128). This indicates that palladium species may have potential provided they are protected from destructive reduction by the choice of suitable ligands. A complex species $[(Ph_3P)_2Pd]_x$ gradually forms in the Ph_3P —Pd metal mixture (128).

Kumada has extended hydrosilylation by phosphine-stabilized complexes into nickel chemistry (173). The most effective catalyst is (XXX). This



thermally stable brown complex also catalyzes H/Cl exchange at Si and the exchange product frequently predominates in the hydrosilylation of 1-alkenes [e.g., Eq. (123)].



Other dichloro(ditertiary phosphine)nickel(II) complexes (see Table VI) catalyze both hydrosilylation and H/Cl exchange, but analogous complexes containing monodentate phosphine ligands or bidentate amine groups are essentially inactive (173).

It is probable that during hydrosilylations these Ni(II) complexes are reduced to π -olefin Ni(0) species which then undergo an oxidative addition in an identical manner to that already discussed for the chloroplatinic acid case. There is current interest in such oxidations (83), and the platinum analog $(\text{Ph}_3\text{P})_2\text{Pt}(\text{olefin})$ has been shown in one case (olefin = C_2H_4) to be an excellent hydrosilylation catalyst (240). In this system, intermediate low oxidation state Pt species have been isolated; their nature is dependent on the electronegativity of the other groups attached to silicon.

Hydrosilylation by Ziegler-type catalyst systems [e.g., $\text{Ni}(\text{acac})_2/\text{AlEt}_3$] has been examined for the reaction of 1-octene with Et_3SiH in benzene (178). Complications include competing isomerization and reduction to metal; however, 1,3-dienes or terminal acetylenes are readily hydrosilylated; with $\text{RC} \equiv \text{CH}$, the major product is $\text{CH}_2:\text{CR}$. $\text{CR}:\text{CHSiX}_3$.

Further material relevant to Section III appears in references 4a, 25a, 45a, 110b, 203c, 229a, 233a, 240b, and 240c.

IV

ORGANOMETALLIC COMPLEXES WITH SILICON-CARBON-TRANSITION METAL BONDS

During 1970 two groups of workers independently drew attention to a type of alkyl ligand which was expected to have significance in transition metal chemistry (78, 239). This may formally be regarded as a carbanion in which one or more α -H atom(s) has been replaced by an organometallic or organic (e.g., *tert*-alkyl, aryl, OR, etc.) group. Illustrations referred mainly to the ligand $\text{Me}_3\text{SiCH}_2^-$.

A. Introduction and General Survey

Transition metal alkyls are often relatively unstable; earlier views had attributed this either to an inherently weak $\text{M}-\text{C}$ bond and/or to the ready homolysis of this bond to produce free radicals. Furthermore, the presence of "stabilizing" π -acceptor ligands such as Cp^- , CO, or R_3P was regarded as almost obligatory. However, (1) the $\text{M}-\text{C}$ bond is not particularly weak compared say to the $\text{M}-\text{N} \lt$ bond, and (2) the presence of the new type of ligand on the metal could make the complex kinetically stable; thus, even "isoleptic" complexes, i.e., compounds of the form MR_n , might be accessible (78, 239). These predictions have largely been borne out (see Table VII).

TABLE VII
 SILYLMETHYL—TRANSITION METAL COMPLEXES

Compounds	Method of preparation ^a (Yield, %)	Comments ^b	References
(Me ₃ SiCH ₂) ₃ Sc·2THF	1 (70)	M.p. 62°–63°; w; monomer in C ₆ H ₆ ; $\nu_{\text{as}}\text{ScC}_3$, 460 cm ⁻¹	176a
(<i>o</i> -MeOC ₆ H ₄ SiMe ₂ CH ₂) ₃ Sc	1 (95)	M.p. 115°–120° (decomp.); c; $\nu_{\text{as}}\text{ScC}_3$, 480 cm ⁻¹	176a
(Me ₃ SiCH ₂) ₄ Ti	1 (73)	M.p. 0°–1°; b.p. ~25°/10 ⁻³ mm Hg; p-y; $\nu_{\text{as}}\text{TiC}_4$, 500 cm ⁻¹ ; monomer in C ₆ H ₆ ; (Me ₃ SiCH ₂) ₃ Ti ⁺ in mass spec.	76, 77
(Me ₂ PhSiCH ₂) ₄ Ti	1 (75)	M.p. ~0°; involatile; p-y; $\nu_{\text{as}}\text{TiC}_4$, 505 cm ⁻¹ ; monomer in C ₆ H ₆ .	77
(MePh ₂ SiCH ₂) ₄ Ti	1 (60)	P-y liquid; $\nu_{\text{as}}\text{TiC}_4$ 480, 520 cm ⁻¹	77
(Me ₃ SiCH ₂) ₂ TiCp ₂	1 (60)	M.p. 185°; o solid; subl. 50°/10 ⁻⁴ mm; $\nu_{\text{as}}\text{TiC}_2$, 444 cm ⁻¹ ; P ⁺	73a, 76, 78, 238, 239
(Me ₃ SiCH ₂) ₄ Zr	1 (73)	M.p. 10°–11°; b.p. ~25°/10 ⁻³ mm Hg; c; pyrophoric; $\nu_{\text{as}}\text{ZrC}_4$, 470 cm ⁻¹ ; monomer in C ₆ H ₆ ; no Zr fragment in mass spec.	76, 77
(PhMe ₂ SiCH ₂) ₄ Zr	1 (66)	M.p. 12°–14°; $\nu_{\text{as}}\text{ZrC}_4$, 475 cm ⁻¹ ; c; monomer in C ₆ H ₆	77
(Me ₃ SiCH ₂) ₂ ZrCp ₂	1 (70)	M.p. 96°–97°; w; $\nu_{\text{as}}\text{ZrC}_2$, 426 cm ⁻¹ ; P ⁺	73a, 76, 78
Me ₃ SiCH ₂ Zr(Cl)Cp ₂	1 (38)	M.p. 118°–121°; p-y; $\nu(\text{ZrC})$, 402 cm ⁻¹	77
(Me ₃ SiCH ₂) ₄ HF	1 (96)	M.p. 8°–10°; b.p. ~50°/10 ⁻³ mmHg; c; pyrophoric; $\nu_{\text{as}}\text{HfC}_4$, 470 cm ⁻¹	176a
(Me ₃ SiCH ₂) ₂ HfCp ₂	1 (50)	M.p. 83°; w	73a, 76, 78
(Me ₃ SiCH ₂) ₄ V	1 (30)	Also from VOCl ₃ (20%); m.p. 43°, d-g; $\nu(\text{VC}_4)$, 504 and 430 cm ⁻¹ ; ν_{max} 15,625 and 23,600 cm ⁻¹ (ϵ 310); μ_{eff} . 1.55 BM at 308° K; ESR	189a
(Me ₃ SiCH ₂) ₃ VO	(50)	By aerial ox. of (Me ₃ SiCH ₂) ₄ V; m.p. 75°; subl. 70°/10 ⁻⁴ mm Hg; p-y; $\nu(\text{VO})$ 985 cm ⁻¹ ; $\nu(\text{VC}_3)$ 522 and 468 cm ⁻¹ ; ν_{max} 26,600 cm ⁻¹	189a, 239

TABLE VII—continued

Compounds	Method of preparation ^a (Yield, %)	Comments ^b	References
(Me ₃ SiCH ₂) ₄ (Me ₃ SiC) ₂ Nb ₂	—	M.p. 152°; r-b; X-ray (Fig. 9) shows Me ₃ SiC bridges which form part of a $\begin{array}{c} \text{Nb} \text{---} \text{C} \text{---} \text{Nb} \text{---} \text{C} \text{ ring} \end{array}$	145
(Me ₃ SiCH ₂) ₄ (Me ₃ SiC) ₂ Ta ₂	—	M.p. 170°; o; isostructural with the Nb complex	145
(Me ₃ SiCH ₂) ₄ Cr	1 (30)	From CrCl ₃ ·3THF; m.p. 40°; subl. 40°/10 ⁻⁴ mm Hg; d-p; $\nu(\text{CrC}_4)$, 536 and 515 cm ⁻¹ ; ν_{max} 19,000 cm ⁻¹ (ϵ 1060); μ_{eff} 2.89 BM at 296° K; ESR	189a, 239
(Me ₃ SiCH ₂) ₆ Mo ₂	1 (15)	From MoCl ₅ ; m.p. 99°; subl. 100°/10 ⁻⁴ mm Hg; y; $\nu(\text{Mo}_2\text{C}_6)$ 534, 484, and 440 cm ⁻¹ ; X-ray (Fig. 10) shows short Mo—Mo (triple?) bond	144, 189a, 239
Me ₃ SiCH ₂ Mo(CO) ₃ Cp	2 (62)	B.p. ~80°/10 ⁻² mm Hg; y liquid; P ⁺	73a, 76, 78
(Me ₃ SiCH ₂) ₆ W ₂	1 (20)	From WCl ₆ ; m.p. 110°; o-b; ν_{max} 21,300 cm ⁻¹ ; isostructural with the Mo complex	144, 189a
Me ₃ SiCH ₂ W(CO) ₃ Cp	2 (55)	M.p. 32°; b.p. ~80°/10 ⁻² mm Hg; y; P ⁺	73a, 75, 76, 78
Me ₂ PhSiCH ₂ W(CO) ₃ Cp	2 (40)	M.p. 47–49°; l	74, 76, 78
Me ₃ SiCH ₂ Mn(CO) ₅	1 (50)	M.p. -5°; b.p. 22°/10 ⁻⁴ mm Hg; y	238, 239
Me ₃ SiCH ₂ Fe(CO) ₂ Cp	1 (70) 2 (59)	M.p. 30°; b.p. 94°/10 ⁻¹ mm Hg; o; P ⁺	74, 164
Me ₃ SiCH ₂ FeCO(PPh ₃)Cp	—	¹ H NMR shows asym. Fe complex; PPh ₃ Et and PPh ₃ Me complexes also mentioned (199)	164, 198, 199
(Me ₃ Si) ₂ CHFe(CO) ₂ Cp	2 (25)	M.p. 98°–100°; y; P ⁺	98
(Me ₃ Si) ₂ CHFeCO(PPh ₃)Cp	(59)	From dicarbonyl + Ph ₃ P; m.p. 124°–125°; o; ¹ H NMR shows asym. Fe complex	98

TABLE VII—continued

Compounds	Method of preparation ^a (Yield, %)	Comments ^b	References
$[(\text{Me}_3\text{SiCH}_2)_2\text{Co}(\text{bipy})_2]^+\text{ClO}_4^-$	1 (70)	M.p. 155°–156° (decomp.); r; ν_{CoC} , 550 cm^{-1}	238
$\text{Me}_3\text{SiCH}_2\text{Ni}(\text{PPh}_3)_2\text{Cp}$	1 (69)	M.p. 121°; g	76, 78, 231
<i>cis</i> -(Me_3SiCH_2) ₂ Pd (PEt ₃) ₂	1 (64)	M.p. 60°–62°; p-y	238
<i>cis</i> -(Me_3SiCH_2) ₂ Pt Pt(PMePh ₂) ₂	1 (75)	M.p. 50°–51°; w; ν_{PtC} , 522 cm^{-1} ; P ⁺	76, 231, 238
<i>cis</i> -(Me_3SiCH_2) ₂ Pt (PMe ₂ Ph) ₂	1 (79)	M.p. 157°; w; $\gamma(^{31}\text{P}$ – ^{195}Pt) shows trans influence of Me_3SiCH_2 similar to Me	74, 76, 78, 231
<i>cis</i> -(Me_3SiCH_2) ₂ Pt (PPh ₃) ₂	1 (77)	M.p. 148°–149°; w	76, 231, 238
<i>cis</i> -(Me_3SiCH_2) ₂ Pt (PEt ₃) ₂	1 (87)	M.p. 88°; w	76, 78, 231
<i>cis</i> -(Me_3SiCH_2) ₂ Pt (AsMePh ₂) ₂	1 (67)	M.p. 135°; w	78, 231
<i>cis</i> -(Me_3SiCH_2) ₂ Pt(dipy)	1 (64)	M.p. 162°–164°; w; ν_{PtC} , 552 cm^{-1}	238
<i>cis</i> -(Me_3SiCH_2) ₂ Pt (cyclo-octadiene)	1 (56)	M.p. 58°–60°; w	238
(Me_3SiCH_2) ₆ Pt ₃ (SMe ₂) ₃	1 (55)	M.p. 130°–135° (decomp.); ν_{PtC} , 542 cm^{-1} ; from <i>cis</i> -(Me_2S) ₂ PtCl ₂ and $\text{Me}_3\text{SiCH}_2\text{Li}$	238
<i>cis</i> - $\text{Me}_3\text{SiCH}_2\text{PtCl}$ (PPhMe ₂) ₂	3 (97)	M.p. 103°; w	76, 78, 231
<i>trans</i> - $\text{Me}_3\text{SiCH}_2\text{PtCl}$ (PPhMe ₂) ₂	4 (42)	M.p. 118°; y; X-ray (Fig. 11) and IR shows trans- influence of Me_3SiCH_2 similar to Me	74, 76, 78, 231
<i>cis</i> - $\text{Me}_3\text{SiCH}_2\text{Pt}$ Cl(PEt ₃) ₂	3 (100)	M.p. 45°; w	76, 78, 231
<i>cis</i> - $\text{Me}_3\text{SiCH}_2\text{PtCl}$ (PPh ₂ Me) ₂	3 (100)	M.p. 172°; w	76, 78, 231
<i>cis</i> - $\text{Me}_3\text{SiCH}_2\text{PtCl}$ (PPh ₃) ₂	3 (28)	M.p. 195°; w	76, 78, 231
<i>cis</i> - $\text{Me}_3\text{SiCH}_2\text{PtCl}$ (AsPh ₂ Me) ₂	3 (100)	M.p. 117°; w	78, 231
<i>cis</i> - $\text{Me}_3\text{SiCH}_2\text{Pt}$ (NO ₃)(PPhMe ₂) ₂	5 (50)	M.p. 80°; w	76, 78, 231
<i>cis</i> - $\text{Me}_3\text{SiCH}_2\text{Pt}(\text{N}_3)$ (PPhMe ₂) ₂	5 (32)	M.p. 99°; w	78, 231

TABLE VII

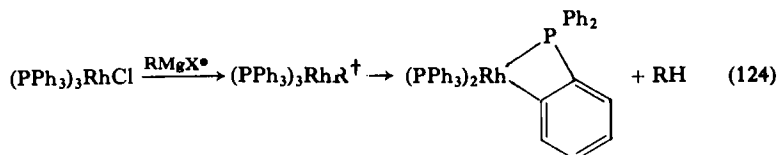
Compounds	Method of preparation ^a (Yield, %)	Comments ^b	References
<i>cis</i> -Me ₃ SiCH ₂ PtBr (PPhMe ₂) ₂	5 (92)	M.p. 113°; w; P ⁺	76, 78, 231
<i>trans</i> -Me ₃ SiCH ₂ Pt Br(PPhMe ₂) ₂	4 (59)	M.p. 131°–133°; y	76, 78, 231
<i>cis</i> -Me ₃ SiCH ₂ Pt Br(PEt ₃) ₂	5 (87)	M.p. 59°; w	76, 78, 231
<i>cis</i> -Me ₃ SiCH ₂ PtBr (PPh ₂ Me) ₂	5 (94)	M.p. 141°	76, 78, 231
<i>cis</i> -Me ₃ SiCH ₂ Pt Br(PPh ₃) ₂	5 (56)	M.p. 225°; w	76, 78, 231
<i>cis</i> -Me ₃ SiCH ₂ PtI (PPhMe ₂) ₂	5 (74)	M.p. 104°; w	78, 231
<i>cis</i> -Me ₃ SiCH ₂ PtI (PEt ₃) ₂	5 (73)	M.p. 66°–68°; w; P ⁺	76, 78, 231
<i>cis</i> -Me ₃ SiCH ₂ PtI (PPh ₃) ₂	5 (100)	M.p. 217°; w	76, 78, 231
Me ₃ SiCHPhPtI(PPh ₃) ₂	6 (25)	M.p. 293°; y	76, 78, 231
Me ₃ SiCH ₂ AuPPh ₃	6 (27)	M.p. 111°–113°	221, 238
Me ₃ SiCH ₂ Cu	1 (75)	M.p. 78°–79° (decomp.); w; tetrameric in C ₆ H ₆ hexameric in cyclohexane; (Me ₃ SiCH ₂ Cu) ₄ ⁺ in mass spec.	176a

^a Numbers refer to the following methods: 1, transition metal chloride + Me₃SiCH₂Li, Me₃SiCH₂MgX, or (Me₃SiCH₂)₂Mg, or related silylmethyl derivative; 2, sodium salt of transition metallate + Me₃SiCH₂X (X usually = I) or related silylmethyl halide; 3, from appropriate (Me₃SiCH₂)₂PtL₂ complex by treatment with HCl in Et₂O; 4, by isomerization of *cis* complex; 5, from chloro complex by displacement of Cl[−] on transition metal with LiBr or NaX in acetone or other solvent; 6, from a Pt⁰ complex and oxidative addition of Me₃SiCH₂I or Me₃SiCHPhI.

^b P⁺ = parent ion detected in mass spectrum. Color of complex: p-y, pale yellow; o, orange; o-b, orange-brown; c, colorless; w, white; d-g, deep-green; b-g, blue-green; r-b, red-brown; d-p, dark-purple; l, lemon; r, red; g, green. ¹H NMR data are available on all the compounds and ³¹P NMR on all the Pt-phosphine complexes (231).

The isoleptic compounds are perhaps of the greatest interest. Thus the complexes (Me₃SiCH₂)₄M [M = Ti, Zr (77), and the paramagnetic V (189a) and Cr (189a, 239)] are moderately stable at ambient temperature, as are the interesting compounds (Me₃SiCH₂)₆M₂ (M = Mo or W) (144, 189a) and (Me₃SiCH₂)₄(Me₃SiC)₂Nb₂ (145). By contrast, Me₄Ti, a rare simple

isoleptic compound, decomposes significantly at -78°C . Likewise, in the series R_2TiCp_2 , thermal stability decreases in the sequence $\text{R} = \text{C}_6\text{F}_5 > \text{Me}_3\text{SiCH}_2 > \text{Ph} > \text{Me} > \text{Et}$ (73a, 77); the ethyl and phenyl derivatives decompose via a β -H-elimination pathway, whereas the others probably reductively eliminate (e.g., $\text{R} = \text{Me}$ gives C_2H_6). When first prepared, the gold compound $\text{Me}_3\text{SiCH}_2\text{AuPPh}_3$ was considered to be less stable than MeAuPPh_3 (221), but upon reexamination this proved to be erroneous (238). However, it is not necessarily the case that β -Si increases overall thermal stability. Thus, attempts to make $\text{Me}_3\text{SiCH}_2\text{Rh}(\text{PPh}_3)_3$ from $(\text{Ph}_3\text{P})_3\text{RhCl}$ and $\text{Me}_3\text{SiCH}_2\text{MgX}$ at low temperature failed [Eq. (124)] (90); the alkane elimination pathway is clearly more accessible for the trimethylsilylmethyl rather than the methyl derivative, and this may be due to steric acceleration and/or the greater solubility of the former compound. Kinetic stabilization



• $\text{R} = \text{Me}$; $\text{X} = \text{Br}$; 0° – 10°C . $\text{R} = \text{Me}_3\text{SiCH}_2$; $\text{X} = \text{Cl}$, I ; 0°C

† Isolated only for $\text{R} = \text{Me}$ (158a), not for $\text{R} = \text{Me}_3\text{SiCH}_2$ (90)

has been stressed also by drawing an analogy between the isoelectronic $[(\text{Me}_3\text{Si})_2\text{N}]_n\text{M}$ and $[(\text{Me}_3\text{Si})_2\text{CH}]_n\text{M}$ (78); the amides are frequently interesting monomers (e.g., $n = 3$ and $\text{M} = \text{Fe}$), whereas the corresponding dimethylamides are polymers [e.g., $\{(\text{Me}_2\text{N})_3\text{Fe}\}_x$]. A wider range of unusual oxidation states and geometries for alkyls may therefore emerge as di- and trisilyl complexes are made, $n = 2$ or 3 in $[(\text{Me}_3\text{Si})_n\text{CH}_{3-n}]_x\text{M}$.

Trimethylsilylmethyl and related complexes $\text{LM}[\text{CY}_m(\text{M}'\text{R}^1\text{R}^2\text{R}^3)_{3-m}]_r$ have been prepared, where M is a transition metal; M' is C, Si, or a Group IVB element; R^1 , R^2 , and R^3 are alkyl or aryl groups; Y is H or an aryl group, and L is the sum of other ligands (if any) attached to the transition metal (76). Fully characterized silicon-containing ($\text{M}' = \text{Si}$) complexes are listed in Table VII. Other compounds have been mentioned, but were not obtained in a pure state: these include $(\text{Me}_3\text{SiCH}_2)_2\text{NbCp}_2$ and $(\text{Me}_3\text{SiCPh}_2)_2\text{Ni}$ (78, 231), $\text{Me}_2\text{PhSiCH}_2\text{TiCl}_3$ (176a), $(\text{CH}_2:\text{CHCH}_2\text{Me}_2\text{SiCH}_2)_n\text{Ti}$ ($n = 3$ or 4) (145a), $[(\text{Me}_3\text{Si})_2\text{CH}]_3\text{Fe}$ (98), $(\text{Me}_3\text{SiCH}_2)_3\text{Y} \cdot 2\text{THF}$ (176a), *trans*- $\text{Me}_3\text{SiCH}_2\text{PtH}(\text{PEt}_3)_2$ (238), and $(\text{Me}_3\text{SiCH}_2)_4\text{Cr}^-$ (189a).

Other features of trimethylsilylmethyl-transition metal chemistry which are noteworthy are (1) the conferment of solubility of metal complexes in nonpolar solvents by ligands such as $\text{Me}_3\text{SiCH}_2^-$ (239), (2) the lability of the Si—C bond in $\text{Me}_3\text{SiCH}_2\text{M}(\text{CO})_3\text{Cp}$ ($\text{M} = \text{Mo}$ or W) to nucleophilic attack (75), (3) the similarity in electronic effect of Me_3SiCH_2 and Me groups, as judged by trans influence studies on $\text{Me}_3\text{SiCH}_2\text{—Pt(II)}$ and Me—Pt(II) compounds (74, 231), and (4) the high catalytic activity of

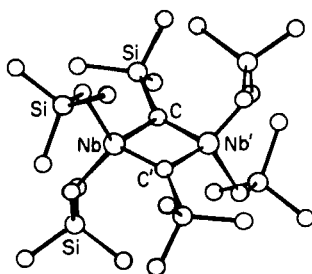


FIG. 9. The molecular structure of $\text{Nb}_2(\text{CSiMe}_3)_2(\text{CH}_2\text{SiMe}_3)_4$. Primed atoms are related to unprimed atoms by a center of symmetry inside the ring. Interatomic distances (Å) and angles (degrees), as follows, are the average of two independent values unless otherwise stated:

Nb—C	1.995(9)	Nb····Nb'	2.897(2)
Nb'—C	1.954(9)	C····C'	2.684(13)
Nb—CH ₃	2.160(9)	Si—C	1.860(13)
(mean of 4)		(mean of 24)	
C—Nb—C'	85.6(4)	Nb—C—Si	119.8(6)
Nb—C—Nb'	94.4(4)	Nb'—C—Si	142.4(5)

$(\text{Me}_3\text{SiCH}_2)_4\text{Ti}$ and related Ti and Zr compounds for α -olefin polymerization (19, 73a). Attention has been drawn to the analogy between $\text{Me}_3\text{—SiCH}_2\text{—M}$ and $\text{PhCH}_2\text{—M}$ chemistry (78): the trimethylsilylmethyl and benzyl ligands share the absence of β -H, and the stabilization of reactive intermediates $\text{XCH}_2\cdot$ or XCH_2^- ($\text{X} = \text{Me}_3\text{Si}$ or Ph).

X-Ray crystallographic data are available for $(\text{Me}_3\text{SiCH}_2)_4(\text{Me}_3\text{SiC})_2\text{Nb}_2$ (145), $(\text{Me}_3\text{SiCH}_2)_6\text{Mo}_2$ (144), and *trans*- $\text{Me}_3\text{SiCH}_2\text{PtCl}(\text{PPhMe}_2)_2$ (74), as illustrated in Figs. 9–11, respectively. The niobium compound is

particularly unusual in having Me_3SiC bridging groups which form part of a four-membered quasi-aromatic M—C—M—C ring, and each Nb has distorted tetrahedral coordination; Nb—CH_2 is 2.160 Å. The molybdenum compound has a very short Mo—Mo distance (2.167 Å), considered as a triple bond. Each Mo is in a distorted tetrahedral environment with the alkyl groups in a staggered conformation and $\text{Mo—CH}_2 = 2.131$ Å. The

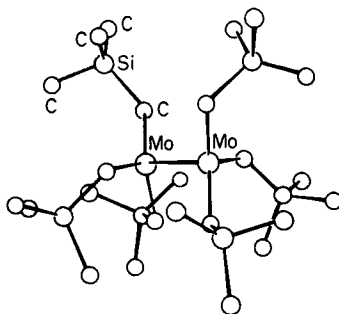


FIG. 10. The molecular structure of $\text{Mo}_2(\text{CH}_2\text{SiMe}_3)_6$.

	No. of independent values	Average bond lengths and bond angles
Mo—Mo	4	2.167 Å
Mo—CH_2	24	2.131 Å
Mo—Mo—CH_2	24	100.6°
$\text{Mo—CH}_2\text{—Si}$	24	121.1°

large SiCH_2Mo angle of 121.1° is probably due to steric repulsion rather than an electronic effect. The Pt—CH_2 distance is 2.079 Å. The Pt—Cl bond length of 2.415 Å suggests that the *trans* influence of $\text{Me}_3\text{SiCH}_2^-$ is large compared with Cl^- but significantly smaller than that of Ph_2MeSi^- , which has a *trans*- Pt—Cl of 2.45 Å (see Section II,D,1).

Trans influence arguments are also based on measurements of $\gamma(^{195}\text{Pt—}^{31}\text{P})$ for *cis*-(Me_3SiCH_2)₂ $\text{Pt}(\text{PPhMe}_2)_2$ and $\nu(\text{PtCl})$ for *trans*- $\text{Me}_3\text{SiCH}_2\text{—PtCl}(\text{PPhMe}_2)_2$ (74), as well as $\gamma(^{195}\text{Pt—H})$ and $\nu(\text{PtH})$ on an uncharacterized specimen of $\text{Me}_3\text{SiCH}_2\text{PtH}(\text{PEt}_3)_2$ (238). These confirm that $\text{Me}_3\text{SiCH}_2^-$ has a high *trans* influence, comparable with that of Me^- .

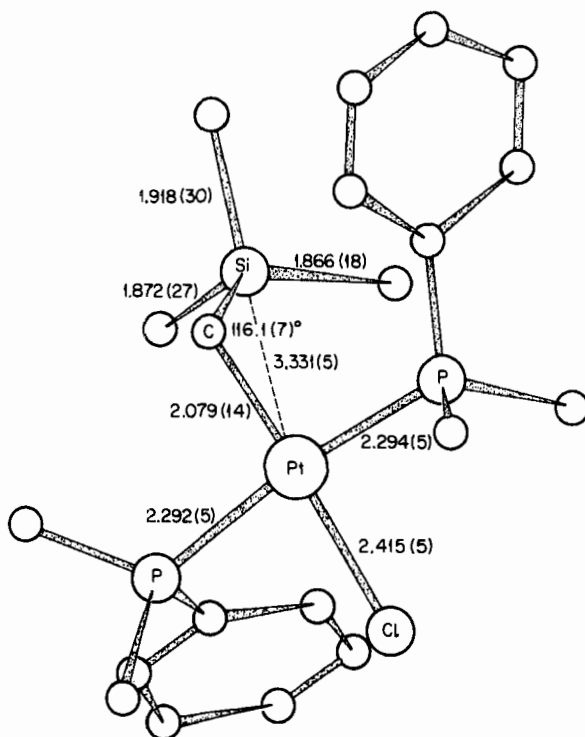


FIG. 11. The molecular structure of *trans*- $\text{Me}_3\text{SiCH}_2\text{PtCl}(\text{PPhMe}_2)_2$.

Spectroscopic studies (IR, Raman, electronic, ESR, and ^1H NMR), as well as bulk magnetic susceptibility measurements [$(\text{Me}_3\text{SiCH}_2)_4\text{M}$ ($\text{M} = \text{V}$ or Cr), $(\text{Me}_3\text{SiCH}_2)_3\text{VO}$, $(\text{Me}_3\text{SiCH}_2)_4\text{Cr}^-$, and $(\text{Me}_3\text{SiCH}_2)_6\text{M}_2$ ($\text{M} = \text{Mo}$ or W)], where appropriate, have been carried out (189a). Factors influencing the stability of transition metal alkyls have also been discussed elsewhere (35a, 188a, 244, 248).

B. The Synthesis of Compounds with Silicon-Carbon-Transition Metal ($\text{RR}'\text{MeSi}-\text{C}-\text{M}$) Bonds

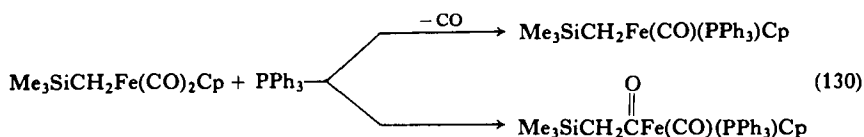
Six methods have been used for the synthesis of $\text{Me}_3\text{SiCH}_2\text{M}$ and related complexes (see Table VII). These all have counterparts in $\text{Me}-\text{M}$ and related chemistry (73). The most widely applicable [e.g., Eq. (125)] is based on a Hal/R exchange using a metal alkyl, e.g., $\text{Me}_3\text{SiCH}_2\text{Li}$,

$\text{Me}_3\text{SiCH}_2\text{MgCl}$, and $(\text{Me}_3\text{SiCH}_2)_2\text{Mg}$ (73a, 77, 78, 231, 238). The most generally recommended reagent is the lithium alkyl; however, it is the strongest reducing agent of the three, which can cause complications, especially for Ti(IV) (73a, 77). The Group IVA complexes readily redistribute R/Hal groups. Diethyl ether is the preferred solvent for the Grignard and RLi reactions, and hexane for the R_2Mg series (77). Reactions are normally carried out at $\sim -30^\circ\text{C}$ to $+20^\circ\text{C}$, depending on the thermal stability of the product. The reactions are usually simple metathetical exchanges. Exceptions are the preparations of $(\text{Me}_3\text{SiCH}_2)_4\text{Cr}$ from a THF solution of CrCl_3 (189a, 239), $(\text{Me}_3\text{SiCH}_2)_4(\text{Me}_3\text{SiC})_2\text{Nb}_2$ from NbCl_5 (144), $(\text{Me}_3\text{SiCH}_2)_6\text{Mo}_2$ from MoCl_5 (189a), and $(\text{Me}_3\text{SiCH}_2)_6\text{W}_2$ from WCl_6 (145, 189a). This synthesis was not effective for $\text{CpM}(\text{CO})_n\text{I}/\text{Me}_3\text{SiCH}_2\text{Li}$ ($\text{M} = \text{Mo}$, $n = 3$; and $\text{M} = \text{Fe}$, $n = 2$) (73a). Metallation of the cyclopentadienyl ligand occurred; in the Fe experiment, ferrocene was a product. For the dichloro-Pt(II) complexes [e.g., $(\text{PPh}_3)_2\text{PtCl}_2$], it proved impossible to isolate a monosubstitution product RPtCl (78, 231); the lower alkylation selectivity with Me_3SiCH_2 than Me is probably due to the high solubility of the silylmethyl monosubstitution products which therefore are alkylated in preference to the sparingly soluble dichloride. The Me_3SiCH_2 and Me groups, of course, have a higher trans effect than Cl.

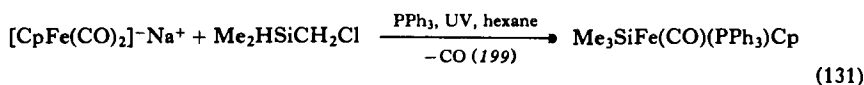
Similarly for the synthesis of monoalkyls of Pt(II) from dialkyls by HCl cleavage of only one Pt—C bond; selectivity for Me_3SiCH_2 is much poorer than for Me derivatives (78, 231), probably for the same reason. The problem was solved by use of a deficiency of HCl in ethereal solution at -78°C [e.g., Eq. (126)], or 1 equivalent of HNO_3 for the nitrate. Selective cleavage of one $\text{Me}_3\text{SiCH}_2\text{—M}$ bond in the Group IVA metallocene dialkyls was not achieved, but a monoalkyl of Zr, $[\text{Me}_3\text{SiCH}_2\text{Zr}(\text{Cl})\text{Cp}_2]$, was obtained as pale yellow crystals by reaction of Cp_2ZrCl_2 with $\text{Me}_3\text{SiCH}_2\text{MgCl}$ in CH_2Cl_2 .

The compound $\text{Me}_3\text{SiCH}_2\text{Fe}(\text{CO})_2\text{Cp}$, the first trimethylsilylmethyl-transition metal complex to be described in the literature (164), was obtained according to Eq. (127) ($\text{M} = \text{Fe}$ and $n = 2$), using tetrahydrofuran as solvent. The method has also been successfully used for Mo and W compounds ($\text{M} = \text{Mo}$ or W , and $n = 3$) (73a, 75). However, a competing reaction, particularly severe for the Mo complex, was the isolation of $\text{CpM}(\text{CO})_3\text{Me}$ as a major product (75). Using Me_3SiCHDI , it was established that the origin of the methyl group on the Mo was the CHDI group and not a Me group on Si. A reaction sequence consistent with the evidence

chloroplatinum(II)—CH₂SiMe₃ complexes, replacing Cl[−] by other anionic ligands (Br[−], I[−], NO₃[−], or N₃[−]), using the appropriate sodium salt (or LiBr) in acetone. The displacement of CO ligand in Me₃SiCH₂Fe(CO)₂Cp by addition of a phosphine is more complicated [Eq. (130)]. Heating under reflux in THF afforded the insertion product (164). However, when the



reaction was carried out under UV irradiation in hexane, the substitution product was formed (199). A further variation was noted in the system according to Eq. (131).



(Me₃SiCH₂)₃VO was obtained not only from VOCl₃ but also by aerial oxidation of (Me₃SiCH₂)₄V on a cellulose column (189a).

Oxidative addition of methyl iodide to coordinatively unsaturated, low-oxidation state *d*⁸ and *d*¹⁰ complexes is an established method for making *d*⁶ and *d*⁸ methylmetal iodides. Me₃SiCH₂I does not react as readily as MeI with (PPh₃)₄Pt (78, 231). (PPh₃)₂Pt(PhCH=CHPh) is more reactive: e.g., *cis*-Me₃SiCH₂PtI(PPh₃)₂ was obtained after 20 hours in C₆H₆ at room temperature.

C. The Reactions of Compounds with Silicon—Carbon—Transition Metal (RR'MeSi—C—M) Bonds

The compounds broadly have the same range of chemistry as the alkyls. The Group IVA (77), VIA (189a), and vanadium (Section IV, B) isoleptic compounds are readily oxidized, but the Cr compound is relatively stable (189a): e.g., (Me₃SiCH₂)₄Zr is pyrophoric (77) as is the V analog (189a); oxidative stability decreases in the series Ti > Zr ~ V and Ph₂MeSiCH₂ > PhMe₂SiCH₂ > Me₃SiCH₂ (77). They also hydrolyze readily, e.g., to give Me₄Si, and this may be used as a method of analysis (77); however, (Me₃SiCH₂)₄Cr and (Me₃SiCH₂)₆Mo₂ are relatively stable, also with

respect to many other reagents (189a). Iodine readily cleaves the M—C bonds quantitatively, and this also has analytical use (77). A complication arises for compounds having aryl—Si—C—M bonds, when the aryl—Si bond is also broken. Silver nitrate in ethanol converts *cis*-Me₃SiCH₂Pt(Cl)-(PPhMe₂)₂ to *cis*-(Me₂PhP)₂Pt(NO₃)₂ (78, 231): preferential Cl⁻/NO₃⁻ exchange might have been expected. Chlorinated alkane solvents also slowly cause C—M cleavage. (Me₃SiCH₂)₄Cr is decomposed by HCl in nonaqueous medium and unstable CrCl₄ is a possible product (189a); (Me₃SiCH₂)₆Mo₂ affords Rb₃Mo₂Cl₈ and Mo(OAc)₂ with 12 *M* HCl/Rb⁺ and glacial HOAc, respectively. Various other reactions have already been discussed in Sections IV,A and IV,B.

The C—M cleavage reaction of Eq. (128) merits further comment. The C—Si bond is normally resistant to nucleophilic cleavage. That it was broken by treating Me₃SiCH₂Mo(CO)₃Cp with [CpMo(CO)₃]⁻Na⁺ at room temperature in THF is therefore surprising (73a, 75). An explanation is that one of the initial products Na⁺[CH₂Mo(CO)₃Cp]⁻ has unexpected stability, as would be the case if the negative charge is delocalized and the complex thus has more the character of an anionic carbene complex than a

TABLE VIII
POLYMERIZATION OF α -OLEFINS BY GROUP IVA
ALKYLS^{a, b}

Catalyst	Olefin	Activity (g/mM/atm/hr)
(Me ₃ SiCH ₂) ₂ TiCp ₂	C ₂ H ₄	0
(Me ₃ SiCH ₂) ₂ ZrCp ₂	C ₂ H ₄	0
(Me ₃ SiCH ₂) ₄ Ti	C ₂ H ₄	1.0
(Me ₃ SiCH ₂) ₄ Zr	C ₂ H ₄	1.0
(Me ₃ SiCHPh) ₄ Zr	C ₂ H ₄	0.1
(Me ₃ SiCH ₂) ₄ Zr/Al ₂ O ₃	C ₂ H ₄	142
α -TiCl ₃ /AlEt ₂ Cl	C ₃ H ₄	20
(Me ₃ SiCH ₂) ₄ Zr/Al ₂ O ₃	C ₃ H ₆ ^c	6.0
α -TiCl ₃ /AlEt ₂ Cl	C ₃ H ₆	4.0

^a From ref. (19).

^b Reaction conditions: PhMe at 80°C; partial pressure of C₂H₄ at 10 atm; [catalyst] = 0.003.

^c Temperature, 65°C; other conditions as in Footnote b.

carbanion. Consistent with this view arylmethylsilanes also have C—Si bonds susceptible to nucleophilic cleavage.

Perhaps the most important chemical property of these complexes is their potential as catalysts, particularly of the early transition metal isoleptic compounds for α -olefin polymerization. This arises because unlike the methyls, they are sufficiently stable to be used at temperatures where polymerization rates are adequate. Some data are summarized in Table VIII (19); π -acceptor ligands are clearly disadvantageous. It will be seen that some of the systems are more active than Ziegler types, although stereoselectivity is poorer.

ACKNOWLEDGMENTS

We thank the S.R.C. for their support of much of our work in this field, Sussex colleagues for their collaboration, especially D. J. Cardin, M. R. Collier, P. J. Davidson, C. Eaborn, S. A. Keppie, K. W. Muir, R. Pearce, G. Speier, S. Takahashi, and Margaret M. Truelock; and Dr. G. Chandra for helpful comments.

REFERENCES

1. Abel, E. W., and Stone, F. G. A., *Quart. Rev., Chem. Soc.* **23**, 325 (1969); **24**, 498 (1970).
2. Adams, D. M., and Chandler, P. J., *Chem. Commun.* 69 (1966).
3. Adams, R. D., and Cotton, F. A., *J. Amer. Chem. Soc.* **92**, 5003 (1970).
4. Amberger, E., Mühlofer, E., and Stern, H., *J. Organometal. Chem.* **17**, P5 (1969).
- 4a. Andrianov, K. A., Rad'kova, O. M., Golubtsov, S. A., and Morozov, N. G., *Zh. Obshch. Khim.* **41**, 1569 (1971).
5. Archer, N. J., Haszeldine, R. N., and Parish, R. V., *Chem. Commun.* 524 (1971).
6. Ash, M. J., Brookes, A., Knox, S. A. R., and Stone, F. G. A., *J. Chem. Soc., A* 458 (1971).
- 6a. Aslanov, L., Mason, R., Wheeler, A. G., and Whimp, P. O., *Chem. Commun.* 30 (1970).
7. Aylett, B. J., *Advan. Inorg. Chem. Radiochem.* **11**, 249 (1968).
8. Aylett, B. J., and Campbell, J. M., *Inorg. Nucl. Lett.* **3**, 137 (1967).
9. Aylett, B. J., and Campbell, J. M., *J. Chem. Soc., A* 1910 (1969).
10. Aylett, B. J., and Campbell, J. M., *J. Chem. Soc., A* 1916 (1969).
11. Aylett, B. J., and Campbell, J. M., *J. Chem. Soc., A* 1920 (1969).
12. Aylett, B. J., Campbell, J. M., and Walton, A., *J. Chem. Soc., A* 2110 (1969).
13. Baay, Y. L., and MacDiarmid, A. G., *Inorg. Nucl. Lett.* **3**, 159 (1967).
14. Baay, Y. L., and MacDiarmid, A. G., *Inorg. Chem.* **8**, 986 (1969).
15. Baird, M. C., *J. Inorg. Nucl. Chem.* **29**, 367 (1967).
16. Baird, M. C., *Progr. Inorg. Chem.* **9**, 1 (1968).
17. Bald, J. F., and MacDiarmid, A. G., *J. Organometal. Chem.* **22**, C22 (1970).
18. Ball, R., Bennett, M. J., Brooks, E. H., Graham, W. A. G., Hoyano, J. K., and Illingworth, S. M., *Chem. Commun.* 592 (1970).
19. Ballard, D. G. H., *23rd Int. Congr. Pure Appl. Chem.* **6**, 213 (1971).

20. Bamford, W. R., Lovie, J. C., and Watt, J. A. C., *J. Chem. Soc., C* 1137 (1966).
21. Bancroft, G. M., Mays, M. J., and Prater, B. E., *J. Chem. Soc., A* 956 (1970).
22. Beck, K. R., and Benkeser, R. A., *J. Organometal. Chem.* **21**, P35 (1970).
23. Benkeser, R. A., Burrows, M. L., Nelson, L. E., and Swisher, J. V., *J. Amer. Chem. Soc.* **83**, 4385 (1961).
24. Benkeser, R. A., and Cunico, R. F., *J. Organometal. Chem.* **6**, 441 (1966).
25. Benkeser, R. A., Dunney, S., Li, G. S., Nerlekar, P. G., and Work, S. D., *J. Amer. Chem. Soc.* **90**, 1871 (1968).
- 25a. Bennett, E. W., and Orenski, P. J., *J. Organometal. Chem.* **28**, 137 (1971).
- 25b. Bennett, M. A., and Patmore, D. J., *Inorg. Chem.* **10**, 2387 (1971).
26. Work by Bennett, M. J., Graham, W. A. G., Hoyano, J. K., and Kaesz, H. D., quoted in *Chem. Eng. News* **48** (24), 75 (1970).
- 26a. Bennett, M. J., and Simpson, K. A., *J. Amer. Chem. Soc.* **93**, 7156 (1971).
27. Benthams, J. E., Craddock, S., and Ebsworth, E. A. V., *J. Chem. Soc., A* 587 (1971).
28. Benthams, J. E., and Ebsworth, E. A. V., *J. Chem. Soc., A* 2091 (1971).
29. Benthams, J. E., and Ebsworth, E. A. V., *Inorg. Nucl. Lett.* **6**, 145 (1970).
30. Berry, A. D., Corey, E. R., Hagen, A. P., MacDiarmid, A. G., Saalfeld, F. E., and Wayland, B. B., *J. Amer. Chem. Soc.* **92**, 1940 (1970).
31. Berry, A. D., and MacDiarmid, A. G., *Inorg. Nucl. Lett.* **5**, 601 (1969).
32. Bibler, J. P., and Wojcicki, A., *Inorg. Chem.* **5**, 889 (1966).
33. Bichler, R. E. J., Booth, M. R., and Clark, H. C., *J. Organometal. Chem.* **24**, 145 (1970).
34. Bichler, R. E. J., and Clark, H. C., *J. Organometal. Chem.* **23**, 427 (1970).
35. Blackmore, T., Cotton, J. D., Bruce, M. I., and Stone, F. G. A., *J. Chem. Soc., A* 2931 (1968).
- 35a. Braterman, P. S., and Cross, R. J., *J. Chem. Soc. (Dalton)* 657 (1972).
36. Breckenridge, J. H., Vandenborn, H. W., and Harris, W. E., *Can. J. Chem.* **49**, 398 (1971).
37. Bressan, M., Favero, G., Corain, B., and Turco, A., *Inorg. Nucl. Lett.* **7**, 203 (1971).
38. Brier, P. N., Chalmers, A. A., Lewis, J., and Wild, S. B., *J. Chem. Soc., A* 1889 (1967).
39. Brookes, A., Knox, S. A. R., and Stone, F. G. A., *J. Chem. Soc., A* 3469 (1971).
40. Brooks, E. H., and Cross, R. J., *Organometal. Chem. Rev. Sect. A* **6**, 227 (1970).
41. Brown, T. L., Edwards, P. A., Harris, C. B., and Kirsch, J. L., *Inorg. Chem.* **8**, 763 (1969).
42. Bruce, M. I., *Advan. Organometal. Chem.* **6**, 273 (1968).
43. Bruce, M. I., Cooke, M., Green, M., and Westlake, D. J., *J. Chem. Soc., A* 987 (1969).
44. Burmeister, J. L., and Edwards, L. M., *J. Chem. Soc., A* 1663 (1971).
45. Calderazzo, F., and Noack, K., *Coord. Chem. Rev.* **1**, 118 (1966).
- 45a. Capka, M., Svoboda, P., Cerny, M., and Hetfleje, J., *Tetrahedron Lett.* 4787 (1971).
46. Cardin, D. J., Cetinkaya, B., Lappert, M. F., Manojlović-Muir, Lj., and Muir, K. W., *Chem. Commun.* 400 (1971).
47. Cardin, D. J., Keppie, S. A., and Lappert, M. F., *J. Chem. Soc., A* 2594 (1970).
48. Cardin, D. J., Keppie, S. A., Kingston, B. M., and Lappert, M. F., *Chem. Commun.* 1035 (1967).
49. Cardin, D. J., Keppie, S. A., Lappert, M. F., Litzow, M. R., and Spalding, T. R., *J. Chem. Soc., A* 2262 (1971).
50. Carey, N. A. D., and Clark, H. C., *Inorg. Chem.* **7**, 94 (1968).
51. Chalk, A. J., *Chem Commun.* 1207 (1969).
52. Chalk, A. J., *J. Organometal. Chem.* **21**, 207 (1970).
53. Chalk, A. J., *Chem. Commun.* 847 (1970).

54. Chalk, A. J., *Trans. N.Y. Acad. Sci.* **32**, 481 (1970).
55. Chalk, A. J., and Harrod, J. F., *J. Amer. Chem. Soc.* **87**, 16 (1965).
56. Chalk, A. J., and Harrod, J. F., *J. Amer. Chem. Soc.* **87**, 1133 (1965).
57. Chalk, A. J., and Harrod, J. F., *J. Amer. Chem. Soc.* **89**, 1640 (1967).
58. Chalk, A. J., and Harrod, J. F., *Advan. Organometal. Chem.* **6**, 119 (1967).
59. Chambers, D. B., Glockling, F., and Light, J. R. C., *Quart. Rev.* **22**, 317 (1968).
60. Charenteney, F. de, Osborn, J. A., and Wilkinson, G., *J. Chem. Soc., A* 787 (1968).
61. Chatt, J., Eaborn, C., and Ibekwe, S. D., *Chem. Commun.* 700 (1966).
62. Chatt, J., Eaborn, C., Ibekwe, S. D., and Kapoor, P. N., *Chem. Commun.* 869 (1967).
63. Chatt, J., Eaborn, C., Ibekwe, S. D., and Kapoor, P. N., *J. Chem. Soc., A* 1343 (1970).
64. Chatt, J., Eaborn, C., and Kapoor, P. N., *J. Organometal. Chem.* **23**, 109 (1970).
65. Chatt, J., Eaborn, C., and Kapoor, P. N., *J. Chem. Soc., A* 881 (1970).
66. Chatt, J., and Shaw, B. L., *J. Chem. Soc.* 5075 (1962).
67. Citron, J. D., Lyons, J. E., and Sommer, L. H., *J. Org. Chem.* **34**, 638 (1969).
68. Cleland, A. J., Fieldhouse, S. A., Freeland, B. H., and O'Brien, R. J., *J. Organometal. Chem.* **32**, C15 (1971).
69. Clemmit, A. F., and Glockling, F., *J. Chem. Soc., A* 2163 (1969).
70. Clemmit, A. F., and Glockling, F., *Chem. Commun.* 705 (1970).
71. Clemmit, A. F., and Glockling, F., *J. Chem. Soc., A* 1164 (1971), and refs. therein.
72. Coates, G. E., and Glockling, F., in "Organometallic Chemistry" (H. Zeiss, ed.), p. 426. Reinhold, New York, 1960.
73. Coates, G. E., Green, M. L. H., and Wade, K., "Organometallic Compounds," Vol. 2. Methuen, London, 1967.
- 73a. Collier, M. R., D. Phil. Thesis, University of Sussex (1971).
74. Collier, M. R., Eaborn, C., Jovanović, B., Lappert, M. F., Manojlović-Muir, Lj., Muir, K. W., and Truelock, M. M., *Chem. Commun.* 613 (1972).
75. Collier, M. R., Kingston, B. M., and Lappert, M. F., *Chem. Commun.* 1498 (1970).
76. Collier, M. R., Kingston, B. M., Lappert, M. F., and Truelock, M. M., British Patent 36021 (1969).
77. Collier, M. R., Lappert, M. F., and Pearce, R., *J. Chem. Soc. (Dalton)* in press (1972).
78. Collier, M. R., Lappert, M. F., and Truelock, M. M., *J. Organometal. Chem.* **25**, C36 (1970); *J. Chem. Soc. (Dalton)*, in press (1973).
- 78a. Collman, J. P., *Trans. N.Y. Acad. Sci.* **30**, 479 (1968).
79. Collman, J. P., *Accounts Chem. Res.* **1**, 136 (1968).
80. Collman, J. P., and Roper, W. R., *J. Amer. Chem. Soc.* **88**, 3504 (1966).
81. Collman, J. P., and Roper, W. R., *Advan. Organometal. Chem.* **7**, 54 (1968).
82. Cook, C. D., and Jauhal, G. S., *Can. J. Chem.* **45**, 301 (1967).
83. Cook, C. D., and Jauhal, G. S., *J. Amer. Chem. Soc.* **90**, 1464 (1968).
84. Corriu, R. J. P., and Masse, J. P., *Chem. Commun.* 213 (1970).
85. Cotton, F. A., and Kraihanzel, C. S., *J. Amer. Chem. Soc.* **84**, 4432 (1962).
86. Cotton, F. A., and Parish, R. V., *J. Chem. Soc.* 1440 (1960).
87. Cotton, F. A., and Wilkinson, G., "Advanced Inorganic Chemistry," 2nd ed., Interscience, London, 1967.
88. Cundy, C. S., Eaborn, C., and Lappert, M. F., *J. Organometal. Chem.* in press (1972).
89. Cundy, C. S., and Lappert, M. F., *Chem. Commun.* 445 (1972).
90. Cundy, C. S., and Lappert, M. F., unpublished results (1971–1972).
91. Curtis, M. D., *J. Amer. Chem. Soc.* **91**, 6011 (1969).
92. Curtis, M. D., *Inorg. Nucl. Lett.* **6**, 859 (1970).
- 92a. Curtis, M. D., *Inorg. Chem.* **11**, 802 (1972).

93. Dalton, J., *Inorg. Chem.* **10**, 1822 (1971).
- 93a. Dalton, J., *Inorg. Chem.* **11**, 915 (1972).
94. Dalton, J., Paul, I., Smith, J. G., and Stone, F. G. A., *J. Chem. Soc., A* 1195 (1968).
95. Dalton, J., Paul, I., Smith, J. G., and Stone, F. G. A., *J. Chem. Soc., A* 1199 (1968).
96. Dalton, J., Paul, I., and Stone, F. G. A., *J. Chem. Soc., A* 1215 (1968).
97. Dalton, J., Paul, I., and Stone, F. G. A., *J. Chem. Soc., A* 2744 (1969).
98. Davidson, P. J., and Lappert, M. F., unpublished work (1972).
99. Delbeke, F. T., Claeys, E. G., and Van der Kelen, G. P., *J. Organometal. Chem.* **25**, 219 (1970), and refs. therein.
100. Delbeke, F. T., Claeys, E. G., Van der Kelen, G. P., and de Caluwe, R. M., *J. Organometal. Chem.* **23**, 497 (1970).
101. Dent, S. P., Eaborn, C., and Pidcock, A., *Chem. Commun.* 1703 (1970).
102. Dent, W., Duncanson, L., Guy, R., Reed, H., and Shaw, B. L., *Proc. Chem. Soc., London* 169 (1961).
103. Dobson, G. R., Jernigen, R. T., and Ross, E. P., *J. Inorg. Nucl. Chem.* **33**, 3375 (1971).
104. Eaborn, C., "Organosilicon Compounds." Butterworths, London, 1960.
105. Eaborn, C., and Bott, R. W., in "Organometallic Compounds of the Group IV Elements" (A. G. MacDiarmid, ed.), Vol. 1, Part 1. Dekker, New York, 1968.
- 105a. Eaborn, C., Kapoor, P. N., Tune, D. J., Turpin, C. L., and Walton, D. R. M., *J. Organometal. Chem.* **34**, 153 (1972).
106. Ebsworth, E. A. V., Lee, A. G., and Sheldrick, G. M., *J. Chem. Soc., A* 1052 (1969).
107. Elder, M., *Inorg. Chem.* **8**, 2703 (1969).
108. Elder, M., *Inorg. Chem.* **9**, 762 (1970).
109. Emerson, K., Ireland, P. R., and Robinson, W. T., *Inorg. Chem.* **9**, 436 (1970).
110. Fieldhouse, S. A., Cleland, A. J., Freeland, B. H., Mann, C. D. M., and O'Brien, R. J., *J. Chem. Soc., A* 2536 (1971).
- 110a. Fink, W., and Wenger, A., *Helv. Chim. Acta* **54**, 2186 (1971).
- 110b. Fink, W., *Helv. Chim. Acta* **54**, 1304 (1971).
111. Gilman, H., Lecture, Queen Mary College, London, 1968.
112. Gilman, H., and Tomasi, R. A., *J. Organometal. Chem.* **15**, 43 (1968).
113. Glockling, F., and Hill, G. C., *J. Chem. Soc., A* 2137 (1971).
114. Glockling, F., and Hooton, K. A., *J. Chem. Soc., A* 1066 (1967).
115. Glockling, F., and Hooton, K. A., *J. Chem. Soc., A* 826 (1968).
- 115a. Glockling, F., and Stobart, S. R., in *Med. Tech. Publ. Co. Int. Rev. Sci.: Inorg. Chem. Ser. One*, Vol. 6, Part 2 (M. J. Mays, ed.), p. 63. Butterworths, London, 1972.
116. Gondal, S. K., MacDiarmid, A. G., Saalfeld, F. E., and McDowell, M. V., *Inorg. Nucl. Lett.* **5**, 351 (1969).
117. Gondal, S. K., MacDiarmid, A. G., Saalfeld, F. E., and McDowell, M. V., *Inorg. Nucl. Lett.* **5**, 413 (1969).
118. Gorsich, R. D., U.S. Patents 3,030,396; 3,030,397; 3,050,537; 3,069,445; and 3,088,814 (1961-1963).
119. Gorsich, R. D., *J. Amer. Chem. Soc.* **84**, 2486 (1962).
120. Graham, W. A. G., and Hart-Davis, A. J., *J. Amer. Chem. Soc.* **93**, 4388 (1971).
121. Graham, W. A. G., Jetz, W., Kummer, R., and Thompson, J. A. J., *Abstr. 50th Meeting Chem. Inst. Can., Toronto*, 1967.
122. Green, M. L. H., and Knowles, P. J., *J. Chem. Soc., A* 1508 (1971).
123. Cross, R. J., *Organometal. Chem. Rev., Sect. A* **2**, 97 (1967).
124. Hagen, A. P., Higgins, C. R., and Russo, P. J., *Inorg. Chem.* **10**, 1657 (1971).
125. Hagen, A. P., and MacDiarmid, A. G., *Inorg. Chem.* **6**, 686 (1967).
126. Hagen, A. P., and MacDiarmid, A. G., *Inorg. Nucl. Lett.* **6**, 345 (1970).

127. Hamilton, R. S., and Corey, E. R., *Abstr. 156th Meeting Amer. Chem. Soc. Atlantic City*, 1968, p. O25.
128. Hara, M., Ohno, K., and Tsuji, J., *Chem. Commun.* 247 (1971).
129. Harrod, J. F., and Chalk, A. J., *J. Amer. Chem. Soc.* **86**, 1776 (1964), and refs. therein.
130. See Chalk and Harrod (56).
131. Harrod, J. F., Gilson, D. F. R., and Charles, R., *Can. J. Chem.* **47**, 2205 (1969).
132. Harrod, J. F., and Smith, C. A., *Can. J. Chem.* **48**, 870 (1970).
133. Harrod, J. F., and Smith, C. A., *J. Amer. Chem. Soc.* **92**, 2699 (1970).
134. Hartley, D., and Ware, M. J., *Chem. Commun.* 912 (1967).
135. Haszeldine, R. N., Parish, R. V., and Parry, D. J., *J. Chem. Soc., A* 683 (1969).
136. Heaton, B. T., and Pidcock, A., *J. Organometal. Chem.* **14**, 235 (1968).
137. Heck, R. F., and Breslow, D. S., *J. Amer. Chem. Soc.* **82**, 4438 (1960).
138. Heck, R. F., and Breslow, D. S., *J. Amer. Chem. Soc.* **83**, 4023 (1961).
139. Hein, F., and Poblath, H., *Z. Anorg. Allgem. Chem.* **248**, 84 (1941).
140. Hengge, E., and Zimmermann, H., *Angew. Chem. Int. Ed. Engl.* **7**, 142 (1968).
- 140a. Highsmith, R. E., Bergerud, J. R., and MacDiarmid, A. G., *Chem. Commun.* 48 (1971).
141. Hooton, K. A., *J. Chem. Soc., A* 1251 (1971).
142. Hoyano, J. K., quoted by Graham, W. A. G., *4th Int. Conf. Organometal. Chem., Bristol*, 1969.
143. Hoyano, J. K., Elder, M., and Graham, W. A. G., *J. Amer. Chem. Soc.* **91**, 4568 (1969).
144. Huq, F., Mowat, W., Shortland, A., Skapski, A. C., and Wilkinson, G., *Chem. Commun.* 1079 (1971).
145. Huq, F., Mowat, W., Skapski, A. C., and Wilkinson, G., *Chem. Commun.* 1477 (1971).
- 145a. Ibekwe, S. D., Parkins, A. W., Lappert, M. F., and Pearce, R., unpublished work (1972).
146. Ibekwe, S. D., and Newlands, M. J. *Chem. Commun.* 144 (1965).
147. Ishikawa, M., and Kumada, M., *Chem. Commun.* 489 (1971), and refs. therein.
148. Jetz, W., and Graham, W. A. G., *J. Amer. Chem. Soc.* **89**, 2773 (1967).
149. Jetz, W., and Graham, W. A. G., *J. Amer. Chem. Soc.* **91**, 3375 (1969).
150. Jetz, W., and Graham, W. A. G., *Inorg. Chem.* **10**, 4 (1971).
151. Jetz, W., and Graham, W. A. G., *Inorg. Chem.* **10**, 1159 (1971).
152. Jetz, W., and Graham, W. A. G., *Inorg. Chem.* **10**, 1647 (1971).
153. Jetz, W., Simons, P. B., Thompson, J. A. J., and Graham, W. A. G., *Inorg. Chem.* **5**, 2217 (1966).
154. Johansson, A. A., Antonova, A. B., Lokshin, B. V., Kolobova, N. E., Anisimov, K. N., and Nesmeyanov, A. N., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 1957 (1969).
155. Kahn, O., and Bigorgne, M., *C. R. Acad. Sci. Ser. C* **263**, 973 (1966).
156. Kahn, O., and Bigorgne, M., *J. Organometal. Chem.* **10**, 137 (1967).
157. Kahn, O., and Bigorgne, M., *C. R. Acad. Sci. Ser. C* **266**, 792 (1968).
158. Kapoor, P. N., D. Phil. Thesis, University of Sussex, 1968.
- 158a. Keim, W., *J. Organometal. Chem.* **14**, 179 (1968).
159. Keppie, S. A., Kingston, B. M., and Lappert, M. F., unpublished results (1969).
160. Keppie, S. A., and Lappert, M. F., *J. Chem. Soc., A* 3216 (1971).
161. Kettle, S. F. A., and Khan, I., *Proc. Chem. Soc., London* 82 (1962).
162. Kettle, S. F. A., and Khan, I., *J. Organometal. Chem.* **5**, 588 (1966).
163. King, R. B., and Pannell, K. H., *Inorg. Chem.* **7**, 1510 (1968).
164. King, R. B., Pannell, K. H., Bennett, C. R., and Ishaq, M., *J. Organometal. Chem.* **19**, 327 (1969).
165. Kingston, B. M., and Lappert, M. F., *Inorg. Nucl. Lett.* **4**, 371 (1968).

166. Kingston, B. M., and Lappert, M. F., *J. Chem. Soc. (Dalton)* 69 (1972).
167. Kiso, Y., Tamao, K., and Kumada, M., *Chem. Commun.* 105 (1972).
168. Knox, S. A. R., Mitchell, C. M., and Stone, F. G. A., *J. Organometal. Chem.* **16**, P67 (1969).
169. Knox, S. A. R., and Stone, F. G. A., *J. Chem. Soc., A* 2559 (1969).
170. Knox, S. A. R., and Stone, F. G. A., *J. Chem. Soc., A* 3147 (1970).
171. Kruck, T., Job, E., and Klose, U., *Angew. Chem. Int. Ed. Engl.* **7**, 374 (1968).
172. Krüerke, U., and Hübel, W., *Chem. Ind. (London)* 1264 (1960).
173. Kumada, M., Kiso, Y., and Umeno, M., *Chem. Commun.* 611 (1970).
174. Kummer, D., and Furrer, J., *Z. Naturforsch. B* **26**, 162 (1971).
175. Kummer, R., and Graham, W. A. G., *Inorg. Chem.* **7**, 523 (1968).
- 175a. Kuz'mina, N. A., Chukovskaya, E. Ts., and Freidlina, R. Kh., *Izv. Akad. Nauk. SSSR Ser. Khim.* 1272 (1967).
176. LaPlaca, S. J., and Ibers, J. A., *Inorg. Chem.* **4**, 778 (1965).
- 176a. Lappert, M. F., and Pearce, R., unpublished results (1972).
177. Lappert, M. F., and Speier, G., *J. Chem. Soc. (Dalton)* in press (1973).
178. Lappert, M. F., and Takahashi, S., *Chem. Commun.* in press (1972).
179. Lewis, J., and Nyholm, R. S., *Sci. Progr.* **52**, 557 (1964).
180. Lukevits, E. Y., and Voronkov, M. G., "Organic Insertion Reactions of Group IVB Elements" (transl. M. J. Newlands). Consultants Bureau, New York, 1966.
181. MacDiarmid, A. G., *Abstr. 3rd Int. Conf. Organometal. Chem. Munich*, 1967.
182. MacDiarmid, A. G., *2nd Int. Symp. Organosilicon Chem. Bordeaux*, 1968.
183. Mann, C. D. M., Cleland, A. J., Fieldhouse, S. A., Freeland, B. H., and O'Brien, R. J., *J. Organometal. Chem.* **24**, C61 (1970).
184. Manojlović-Muir, Lj., Muir, K. W., and Ibers, J. A., *Inorg. Chem.* **9**, 447 (1970).
185. Margrave, J. L., Williams, D. L., and Wilson, P. W., *Inorg. Nucl. Lett.* **7**, 103 (1971) and refs. therein.
186. Markby, R., Wender, I., Friedel, R., Cotton, F. A., and Sternberg, H., *J. Amer. Chem. Soc.* **86**, 6529 (1958).
187. Marks, T. J., and Seyam, A. M., *J. Organometal. Chem.* **31**, C62 (1971).
188. McWeeny, R., Mason, R., and Towl, A. D. C., *Discuss. Faraday Soc.* **47**, 20 (1969).
- 188a. Mingos, D. P. M., *Chem. Commun.* 165 (1972).
189. Morrison, D. L., and Hagen, A. P., *Inorg. Synth.* **13**, 65 (1971).
- 189a. Mowat, W., Shortland, A., Yagupsky, G., Hill, N. J., Yagupsky, M., and Wilkinson, G., *J. Chem. Soc. (Dalton)* 533 (1972).
190. Muir, K. W., *J. Chem. Soc., A* 2663 (1971).
191. Muir, K. W., and Ibers, J. A., *Inorg. Chem.* **9**, 440 (1970).
- 191a. Nasta, M. A., and MacDiarmid, A. G., *J. Organometal. Chem.* **18**, P11 (1969).
192. Nasta, M. A., and MacDiarmid, A. G., *J. Amer. Chem. Soc.* **93**, 2813 (1971).
- 192a. Nasta, M. A., MacDiarmid, A. G., and Saalfeld, F. E., *J. Amer. Chem. Soc.* **94**, 2449 (1972).
193. Nesmeyanov, A. N., Anisimov, K. N., Kolobova, N. E., and Denisov, F. S., *Izv. Akad. Nauk SSR Otd. Khim. Nauk* 1419 (1968).
194. Nesmeyanov, A. N., Anisimov, K. N., Kolobova, N. E., and Skripkin, V. V., *Izv. Akad. Nauk SSSR Otd. Khim. Nauk* 2364 (1967).
195. Nicholson, B. K., and Simpson, J., *J. Organometal. Chem.* **32**, C29 (1971).
196. Noll, W., "Chemistry and Technology of Silicones." Academic Press, New York, 1968.
- 196a. Ogino, K., and Brown, T. L., *Inorg. Chem.* **10**, 517 (1971).

- 196b. Oliver, A. J., and Graham, W. A. G., *Inorg. Chem.* **10**, 1 (1971).
197. Osborn, J. A., Jardine, F. H., Young, J. F., and Wilkinson, G., *J. Chem. Soc., A* 1711 (1966) and refs. therein.
198. Pannell, K. H., *Chem. Commun.* 1346 (1969).
199. Pannell, K. H., *J. Organometal. Chem.* **21**, P17 (1970).
200. Parshall, G. W., *Accounts Chem. Res.* **3**, 139 (1970).
201. Patil, H. R. H., and Graham, W. A. G., *Inorg. Chem.* **5**, 1401 (1966).
202. Patmore, D. J., and Graham, W. A. G., *Inorg. Chem.* **5**, 2222 (1966).
203. Piper, T. S., Lemal, D., and Wilkinson, G., *Naturwissenschaften* **43**, 129 (1956).
- 203a. Pomeroy, R. K., Gay, R. S., Evans, G. O., and Graham, W. A. G., *J. Amer. Chem. Soc.* **94**, 272 (1972).
- 203b. Pomeroy, R. K., and Graham, W. A. G., *J. Amer. Chem. Soc.* **94**, 274 (1972).
- 203c. Pukhnarevich, V. B., Sushchinskaya, S. P., Trofimov, B. A., and Voronkov, M. G., *Zh. Obshch. Khim.* **41**, 1879 (1971).
204. Reikhsfel'd, V. O., Astrakhanov, M. I., and Kagan, E. G., *Zh. Obshch. Khim.* **40**, 699 (1970).
205. Robiette, A. G., Sheldrick, G. M., Simpson, R. N. F., Aylett, B. J., and Campbell, J. M., *J. Organometal. Chem.* **14**, 279 (1968).
206. Robinson, W. T., and Ibers, J. A., *Inorg. Chem.* **6**, 1208 (1967).
207. Ross, E. P., and Dobson, G. R., *Chem. Commun.* 1229 (1969).
208. Ryan, J. W., and Speier, J. L., *J. Amer. Chem. Soc.* **86**, 895 (1964).
209. Rylander, P. N., *Engelhard Ind. Tech. Bull.* **10**, 130 (1970).
210. Saalfeld, F. E., McDowell, M. V., Hagen, A. P., and MacDiarmid, A. G., *Inorg. Chem.* **7**, 1665 (1968).
211. Saalfeld, F. E., McDowell, M. V., Gondal, S. K., and MacDiarmid, A. G., *Inorg. Chem.* **7**, 1465 (1968).
212. Saalfeld, F. E., McDowell, M. V., and MacDiarmid, A. G., *J. Amer. Chem. Soc.* **92**, 2324 (1970).
213. Saalfeld, F. E., McDowell, M. V., and MacDiarmid, A. G., "Recent Developments in Mass Spectroscopy," p. 1073. (1971).
214. Sakurai, H., Okada, A., Kira, M., and Yanezawa, K., *Tetrahedron Lett.* 1511 (1971).
215. Schmid, G., and Balk, H.-J., *Ber.* **103**, 2240 (1970).
216. Schneider, M. L., Shearer, H. M. M., Glockling, F., and McGregor, A., *J. Inorg. Nucl. Chem.* **32**, 3101 (1970).
- 216a. Schrauzer, G. N., and Kratel, G., *Angew. Chem. Int. Ed. Engl.* **4**, 146 (1965).
217. Schrieke, R. R., and West, B. O., *Aust. J. Chem.* **22**, 49 (1969).
218. Schrieke, R. R., and West, B. O., *Inorg. Nucl. Lett.* **5**, 141 (1969).
219. Selin, T. G., and West, R., *J. Amer. Chem. Soc.* **84**, 1863 (1962).
220. Seyferth, D., and Kahlen, N., *J. Amer. Chem. Soc.* **82**, 1080 (1960).
221. Shiotani, A., and Schmidbaur, H., *J. Amer. Chem. Soc.* **92**, 7003 (1970).
222. Skapski, A. C., and Troughton, P. G. H., *Chem. Commun.* 1230 (1968).
223. Sommer, L. H., and Lyons, J. E., *J. Amer. Chem. Soc.* **90**, 4197 (1968).
224. Sommer, L. H., Lyons, J. E., and Fujimoto, H., *J. Amer. Chem. Soc.* **91**, 7051 (1969).
225. Sommer, L. H., Pietrusza, E. W., and Whitmore, F. C., *J. Amer. Chem. Soc.* **69**, 188 (1947).
226. Spalding, T. R., "Spectroscopic Methods in Organometallic Chemistry" (W. O. George, ed.), p. 95. Butterworths, London, 1970.
227. Spencer, D. D., *Diss. Abstr. B* **31**, 573 (1970).
228. Stone, F. G. A., in "New Pathways in Inorganic Chemistry" (E. A. V. Ebsworth,

- A. G. Maddock, and A. G. Sharpe, eds.). Cambridge Univ. Press, London and New York, 1968.
229. Takahashi, S., Shibano, T., and Hagihara, N., *Chem. Commun.* 161 (1969).
- 229a. Takahashi, S., Shibano, T., Kojima, H., and Hagihara, N., *Organometal. Chem. Syn.* 1, 193 (1970).
230. Treichel, P. M., Shubkin, R. L., Barnett, K. W., and Reichard, D., *Inorg. Chem.* 5, 1177 (1966).
231. Truelock, M. M., D. Phil. Thesis, University of Sussex (1971).
232. Ugo, R., *Engelhard Ind. Tech. Bull.* 11, 45 (1970).
233. Vaska, L., *Accounts Chem. Res.* 1, 335 (1968).
- 233a. Voronkov, M. G., Pukhnarevich, V. B., Sushchinskaya, S. P., Kopylova, L. I., and Trofimov, B. A., *Zh. Obshch. Khim.* 41, 2102 (1971).
234. Vyazankin, N. S., Razuvaev, G. A., and Kruglaya, O. A., *Organometal. Chem. Rev., Sect. A* 3, 323 (1968).
- 234a. Walton, A., Ph.D. Thesis, London (1971).
235. Watters, K. L., Brittain, J. N., and Risen, W. M., *Inorg. Chem.* 8, 1347 (1969).
236. Wilke, G., and Schott, M., *Angew. Chem. Int. Ed. Engl.* 5, 583 (1966).
237. Wittle, J. K., and Urry, G., *Inorg. Chem.* 7, 560 (1968).
238. Wozniak, B., Ruddick, J. D., and Wilkinson, G., *J. Chem. Soc., A* 3116 (1971).
239. Yagupsky, G., Mowat, W., Shortland, A., and Wilkinson, G., *Chem. Commun.* 1369 (1970).
240. Yamamoto, K., Hayashi, T., and Kumada, M., *J. Organometal. Chem.* 28, C37 (1971).
- 240a. Yamamoto, K., Okinoshima, H., and Kumada, M., *J. Organometal. Chem.* 23, C7 (1970).
- 240b. Yamamoto, K., Hayashi, T., and Kumada, M., *J. Amer. Chem. Soc.* 93, 5301 (1971).
- 240c. Yamamoto, K., Uramoto, Y., and Kumada, M., *J. Organometal. Chem.* 31, C9 (1971).
241. Young, J. F., *Advan. Inorg. Chem. Radiochem.* 11, 92 (1968).

REFERENCES ADDED IN PROOF

242. Ang, H. G., and Lau, P. T., *Organometal. Chem. Rev. Sect. A* 8, 235 (1972).
243. Belluco, U., Deganello, G., Pietropaola, R., and Uguagliati, P., *Inorg. Chim. Acta Rev.* 4, 7 (1970).
244. Braterman, P. S., *J. Chem. Soc. Chem. Commun.* 761 (1972).
245. Cheney, A. J., Mann, B. E., Shaw, B. L., and Slade, R. M., *J. Chem. Soc., A* 3833 (1971).
246. Gilmore, C. J., and Woodward, P., *J. Chem. Soc. (Dalton)* 1387 (1972).
247. Graham, W. A. G., personal communication (1972).
248. Haszeldine, R. N., and Parish, R. V., personal communication (1972).
249. Wilkinson, G., *Pure and Appl. Chem.* 30, 627 (1972).

Preparation and Reactions of Organocobalt (III) Complexes

J. M. PRATT

Imperial Chemical Industries Ltd.
Corporate Laboratory
Runcorn, Cheshire, England

P. J. CRAIG

School of Chemistry
City of Leicester Polytechnic
Leicester, Leics, England

I. Introduction	332
A. Aims of the Review	332
B. Nomenclature and Structure of the Ligands	336
II. Coordination Chemistry	341
A. Valency and Spin State	341
B. Stereochemistry	343
C. Cis and Trans Effects	349
D. <i>d-d</i> Spectra	350
III. Formation of the Co—C Bond	350
A. Reactions of Co(I) and Co—H Complexes	351
B. Reactions of Co(II) Complexes	358
C. Reactions of Co(III) Complexes	360
IV. Preparative Methods	361
A. Corrinoids	384
B. Other Macrocyclic Complexes	386
C. Penta- and Tetracyanides	394
V. Reactions and Equilibria Not Involving Cleavage of the Co—C Bond	396
A. Acid/Base Equilibria	396
B. Irreversible Reactions	397
C. σ - π Equilibria	399
VI. Cleavage of the Co—C Bond	401
A. Photochemical Reactions	403
B. Simple Thermal Reactions	405
C. Transfer Reactions	421
D. Insertion and Elimination Reactions	427
E. Oxidation and Reduction	432
VII. Catalytic and Enzymatic Reactions	433
A. Homogeneous Hydrogenation Catalyzed by Cobalt Cyanide Complexes	433
B. Other Catalytic Reductions and Hydrogenations	437
C. Exchange and Isomerization	438
D. Enzymatic Reactions	439
References	441

I

INTRODUCTION

A. Aims of the Review

The last decade or so has seen the birth and rapid development of the field of organocobalt(III) complexes, which has come to occupy an unusual position, linking together organometallic chemistry, coordination chemistry, and even biochemistry. The great interest in vitamin B₁₂ has perhaps tended to overemphasize the biochemical relevance of these complexes and to obscure their importance to the development of organometallic chemistry. The present interest in organo-transition metal chemistry, which can be dated back to the discovery of ferrocene in 1951, has centered mainly on compounds or complexes which contain π -bonding olefins, acetylenes, and cyclopentadienyls, and in which the other ligands usually include CO or phosphines and the metal has a relatively low valency and often an unusual configuration. By contrast, the organocobalt(III) complexes contain σ -bonded carbanions, the other ligands are usually coordinated through nitrogen, the metal has a relatively high valency, and the complex a fairly regular stereochemistry (octahedral or square pyramidal). These are, of course, the properties which enable them to be treated as coordination complexes. The development of organocobalt(III) chemistry has therefore extended our knowledge of organometallic compounds containing σ -bonded organic groups and is complementary to the more traditional work on π -bonded ligands. The fusion of these two approaches and their application to other transition metals should lead to extensive new areas of organometallic chemistry.

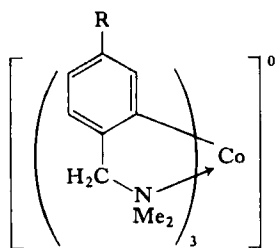
There have, in fact, been two rather separate strands in the development of organocobalt(III) chemistry. One dates from 1961, when Lenhert and Hodgkin (115, 114) reported the results of their X-ray analysis of the so-called coenzyme form of vitamin B₁₂, in which they showed that one of the axial ligands was a substituted alkyl group [see Structure (II)]. It was soon shown that the compound was diamagnetic and could be regarded as a cobalt(III) complex with a coordinated carbanion (85, 86). This discovery stimulated interest in the preparation and study both of other organocobalt corrinoids (derivatives of vitamin B₁₂) and of a much wider range of organocobalt(III) complexes in which the equatorial coordination positions are occupied by chelating ligands such as porphyrin, salen, and bis-DMG

(for nomenclature and structures, see Section I,B). The driving force behind this work has been the attempt to elucidate the mechanism of the enzymatic reactions by studying the reactions of "model" compounds. The second strand has a longer history. In 1942 Iguchi discovered that aqueous solutions of cobalt(II) salts in excess cyanide will absorb hydrogen and will catalyze the homogeneous hydrogenation of organic compounds such as isatin and cinnamic acid, but no solid complexes were isolated (92, 93). In 1959 Griffith and Wilkinson isolated the binuclear complex $[(\text{NC})_5\text{CoCH}=\text{CHCo}(\text{CN})_5]^{6-}$ from the reaction of acetylene with the pentacyanocobalt(II) ion (70), while Halpern and Maher in 1964 (74) and Kwiatek and Seyler in 1965 (109, 110) prepared and isolated mononuclear complexes of the type $[\text{Co}(\text{CN})_5\text{R}]^{3-}$, where R is an alkyl or aryl group. Since then many other such organopentacyanocobalt complexes have been prepared, usually only in solution [see the review by Kwiatek (105)]. The interest in these cyanide complexes has centered on the mechanism of the catalyzed homogeneous hydrogenation reactions. The organopentacyanides do, however, show many similarities to the other groups of complexes in their chemical reactions, and a comparison of all these complexes helps to build up a more complete picture of the chemical and physical properties of organocobalt(III) complexes as a whole.

Organocobalt(III) complexes have now been prepared with a very wide range of unidentate organo-ligands and quite a variety of other equatorial and axial ligands; for examples of these ligands see Section I,B. The organo-corrinoids alone probably include a greater variety of σ -bonded carbanions than any other comparable group of organometallic complexes, together with the first known naturally occurring organometallic complexes. The preparative methods (see Sections III and IV) include a greater choice than is usual in organometallic chemistry, the reactions are often simpler and the yields higher, and the reactions can in many cases be carried out in aqueous solution. These complexes offer interesting possibilities for the preparative organometallic chemist to apply new reagents and reactions, and to study compounds which are generally stable to both air and moisture and often soluble in water. They show reactions involving radical, carbonium ion and carbanion intermediates and, except in the case of the pentacyanides, these reactions are not complicated by reactions between the organo-ligand and ligands in the cis position [contrast the insertion reactions of $\text{RCo}(\text{CO})_4$]. Most or all organocobalt(III) complexes undergo photochemical reactions, and some are involved as intermediates in catalytic reactions, e.g., the

corrinoids in enzymatic reactions and the pentacyanides in homogeneous hydrogenation. These cobalt(III) complexes, in particular the corrinoids, have also provided an excellent opportunity for comparing the effects of the organo-ligands on the properties of other ligands in the complex (i.e., their *cis* and *trans* effects) with those of ligands such as H_2O , NH_3 , Cl^- , and CN^- , which are more commonly studied by coordination chemists. The effects of organo-ligands on the *d-d* spectra can best be studied in the pentacyanide complexes, but relatively little work has yet been reported. The development of the chemistry of organocobalt(III) complexes over the last decade is, therefore, of interest to organometallic chemists, coordination chemists and photochemists, and to biochemists and industrial chemists.

This review is concerned exclusively with complexes which can formally be regarded as cobalt(III) compounds containing a single (or very occasionally two) σ -bonded organo ligands (i.e., carbanions, whether alkyl, aryl, acyl, alkenyl, alkynyl, etc.) occupying a single coordination position. We, therefore, exclude organocobalt(III) complexes with the following types of ligands: (1) Neutral π -bonding ligands such as CO and RNC. (2) π -bonding carbanions occupying more than one coordination position, such as π -cyclopentadienyl and π -allyl, e.g. $[\text{Co}(\text{bipy})(\pi\text{-2-butenyl})_2]^+$ (123) and $[\text{Co}(\pi\text{-allyl})_2\text{Cl}]$ (178); however, we include the π -allyltetracyanide complexes because they are formed reversibly from the σ -alkenylpentacyanide complexes (see Section V,C). (3) Chelating carbanions as in the complexes of structure (I) (36); but we include bridging bidentate carbanions as in $[(\text{NC})_5\text{Co}-\text{CH}=\text{CH}-\text{Co}(\text{CN})_5]^{6-}$. (4) We have excluded the hexacetylides $[\text{Co}(\text{C}\equiv\text{CR})_6]^{3-}$, which are best considered as analogs of the hexacyanides $[\text{Co}(\text{CN})_6]^{3-}$, but include those complexes which contain only one acetylide per cobalt. (5) Complexes such as $[(\pi\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_2(\text{PPh}_3)]$ (182) and *cis*- $[\text{Co}(\text{bipy})_2(\text{CH}_3)_2]$ (123) are borderline cases; they have, perhaps rather arbitrarily, been excluded from the text of the review and

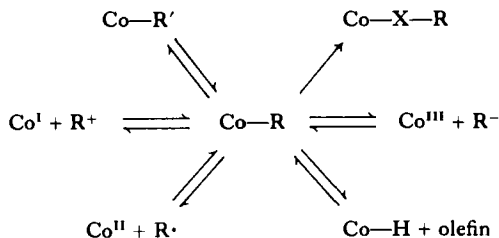


(I)

are mentioned here only for the sake of completeness. The remaining types of organocobalt(III) complexes form a reasonably homogeneous group with a number of features in common.

These complexes may be either six-coordinate with an octahedral configuration or five-coordinate with a square-pyramidal configuration, in which the organo ligand occupies the apical position; a few form dimers through the interaction of each cobalt with a coordinated atom of the equatorial ligand of the other half (see Section II,B,1). In virtually all groups of complexes four "equatorial" coordination positions are occupied by a tetradentate ligand (e.g., corrin, salen) or equivalent ligand (e.g., bis-DMG, in which two bidentate DMG ligands are joined by hydrogen bonds into a planar tetradentate ligand); the only exceptions are the organopentacyanides. The donor atoms of these tetradentate ligands are N_4 or N_2O_2 and, except in the case of CR where one nitrogen atom is tetrahedral, all form part of a conjugated system; the structures of these ligands are shown in Section I,B. One hopes and expects that the range of equatorial ligands may be extended in the future (e.g., to include S and P as donor atoms).

The main aim of this review is to survey the reactions by which the Co—C bond is made, broken, or modified, and which may be used for preparative purposes or be involved in catalytic reactions. Sufficient evidence is now available to show that there exists a general pattern of reactions by which the Co—C bond can be made or broken and in which the transition state may correspond to Co(III) and a carbanion (R^-), Co(II) and a radical (R^\cdot), Co(I) and a carbonium ion (R^+), or a cobalt hydride (Co—H) and an olefin. Reactions are also known in which the organo ligand (R) may be reversibly or irreversibly modified (to R') without cleavage of the Co—C bond, or in which insertion occurs into the Co—C bond (to give Co—X—R). These reactions can be shown schematically as follows:



Certain groups of organocobalt(III) complexes have been dealt with in previous reviews. The organo-corrinoids have been mentioned in all reviews on vitamin B₁₂ since 1961, when the coenzyme form was identified as an organometallic compound [see, for example, (79, 178) and references therein]. The literature on the corrinoids is too extensive to be treated comprehensively here and for details and references readers are referred to the book on *The Inorganic Chemistry of Vitamin B₁₂* (136); certain other aspects of the organometallic chemistry of cobalt corrinoids are treated elsewhere (137). The pentacyanides were reviewed in 1967 (105), the DMG complexes (cobaloximes) in 1968 (145), and some aspects of salen, BAE, and related complexes in 1970 (17).

B. Nomenclature and Structure of the Ligands

The term "organo-ligand" is used here to designate all ligands which are coordinated to the cobalt through a formally negatively charged carbon atom, *except* cyanide. For the purposes of distributing the charge, the cobalt ion is considered to be trivalent, i.e., the doubly charged $[\text{CoCH}_3]^{2+}$ unit is treated as a complex of the cobalt(III) ion with the organo-ligand CH_3^- . This term does not include neutral ligands such as CO or RNC.

The following letters are used in formulas and equations to denote different types of ligands:

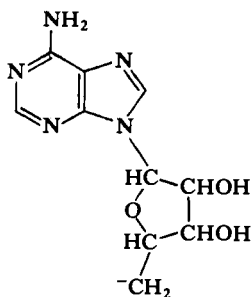
R	An organo-ligand
L ₄	The equatorial ligand(s)
X, Y	Other axial ligands, neutral or anionic.
B	Neutral base or axial ligand, used where it is necessary to distinguish a neutral (B) from an anionic ligand or a halide (both X).

Common abbreviations used here include: py (pyridine), pip (piperidine), THF (tetrahydrofuran), DMF (dimethylformamide), etc. Some others are given in Table III.

The formulas and names of these organocobalt complexes are usually given in the form $[\text{RCo}(\text{L}_4)\text{X}]$, e.g., $[\text{vinyl-Co}(\text{salen})\text{py}]$.

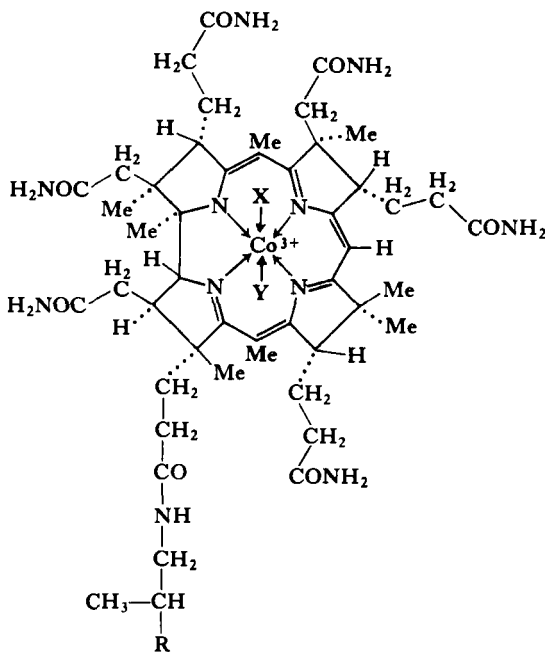
Some surprisingly large and unwieldy organo ligands have been used in the corrinoids [for examples and references see (136)]. Of particular interest is the 5-deoxyadenosyl ligand (II) present in some of the naturally occurring forms.

Most of the tetradentate equatorial ligands have a complex structure and, since their systematic names are often cumbersome, abbreviations and



(II)

trivial names are commonly used. In two cases the cobalt complexes themselves may have an additional trivial name (e.g., salcomine, cobaloxime) which is different from the abbreviation for the ligand alone [salen, (DMG)₂]. Different abbreviations for the same ligand are often used by different authors, and occasionally even by the same authors. In addition, certain of the abbreviations may show no obvious connection with the systematic name of the ligand. It is to be hoped that these abbreviations may be given a more logical basis some time in the future. In the list below we give the ligands with the structure and charge which they possess when co-ordinated

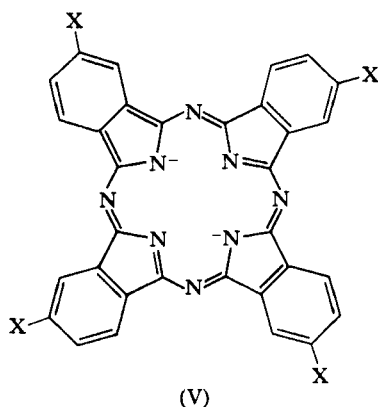
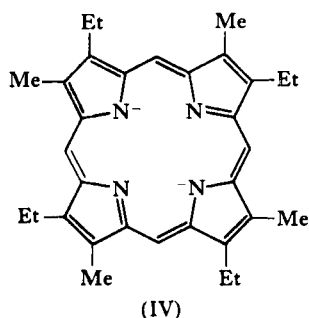


(IIIa)

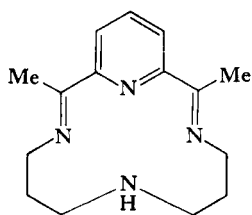
to the cobalt ion, together with the abbreviation adopted here (in *italics*) and any other abbreviations which may be met in papers quoted in this review.

The cobalt corrinoids are derivatives of vitamin B₁₂. A wide variation is observed in the nature of the side chains in the naturally occurring and, of course, in the synthetically modified derivatives. But here we need be concerned only with the two groups of cobalt corrinoids, which have structure (IIIa) where R = OH (called "cobinamides") and R is the nucleotide (IIIb) linked via the phosphate ("cobalamins"). In the cobalamins the free nitrogen of the heterocyclic base (4,6-dimethylbenziminazole) in the nucleotide is usually coordinated to the cobalt in position Y. The other axial ligands may be H₂O, CN⁻, CH₃⁻, etc., and are named first, e.g., cyanoaquocobinamide, cyanocobalamin (vitamin B₁₂ itself), methylcobalamin, 5-deoxyadenosylcobalamin [the organometallic complex with the ligand (II)]. Organometallic complexes are, in fact, known with other corrinoid ligands, but these show no important differences from the cobinamides and cobalamins and will not be mentioned in this review; for further details see (136). The following abbreviations are used here:

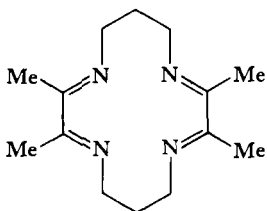
corrinoids in general	<i>corrin</i>
cobalamins	<i>cobal</i>
cobinamides	<i>cobin</i>



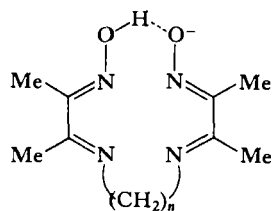
Aetioporphyrin I	<i>porph</i>	X = H	Phthalocyanine	<i>phthal</i> , Pc
		X = SO ₃ H	Phthalocyaninetetrasulfonic acid	<i>phthalTS</i> , TsPc
			(N.B. The substituents all occupy β -positions, but their disposition relative to each other is not known.)	



(VI)

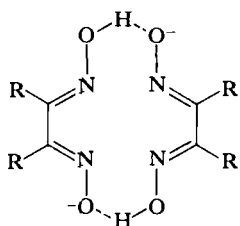
CR, *Cr*, *cyp*

(VII)

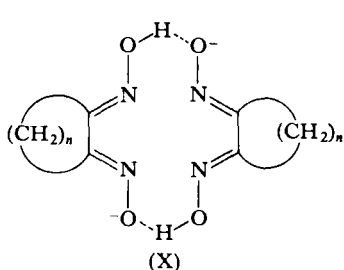
tim

(VIII)

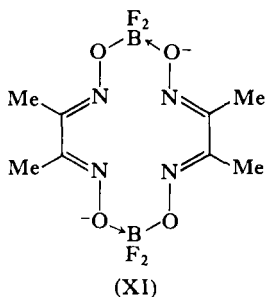
$n = 2$ (*DO*) (*DOH*) *en*, *Dmed*⁺
 $n = 3$ (*DO*) (*DOH*) *pn*,
 (*DOH*) (*DO*) *pn*, *Dmpd*⁺



(IX)

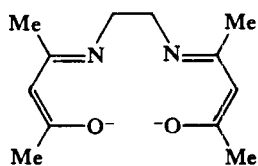
 $R = H$ (*G*)₂, *glyoxime* $R = Me$ bis(dimethylglyoximate),*(DMG)*₂, (*dmg*)₂, (*dmgh*)₂, *dmgh*₂, (*dmgH*)₂*Dmg*, (*DH*)₂, (*D₂H₂*), (*DMH*)₂, *bdg* $R = \text{phenyl}$ (*DPG*)₂, *Dpg*, (*DPH*)₂ $R = p\text{-methoxyphenyl}$ (*DMPG*)₂, (*DMPH*)₂ $R = p\text{-nitrophenyl}$ (*DNPG*)₂, (*DNPH*)₂

(X)

 $n = 3$ (*CPD*)₂ $n = 4$ (*CHD*)₂, *Chdioxime*

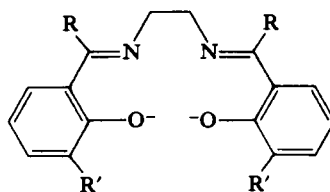
(XI)

*(DMG-BF₂)*₂, *DmgB₂F₄*



(XII)

The abbreviations are derived from the trivial name of the free base, viz., bis(acetylacetonate)ethylenediamine, *BAE*, bae, acen

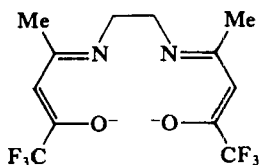


(XIV)

R, R' = H. The abbreviations are derived from the trivial name of the free base, viz., bis(salicylaldehyde)ethylenediamine, *salen*, *SALEN*, *SaEn*

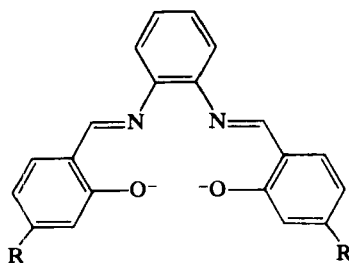
R = Me, R' = H *7-Me-salen*, *Me₂salen*, *7,7'-(CH₃)₂-salen*, *oiafen*.

R = phenyl, R' = H *7-Ph-salen*



(XIII)

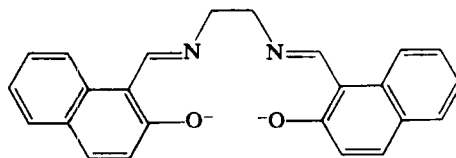
tfen



(XV)

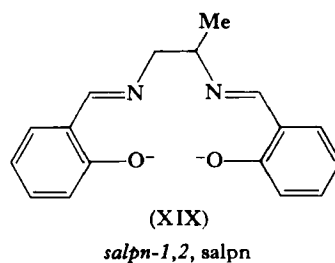
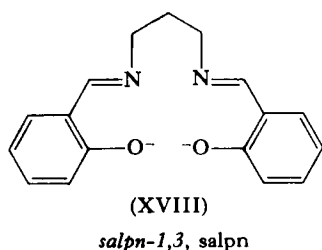
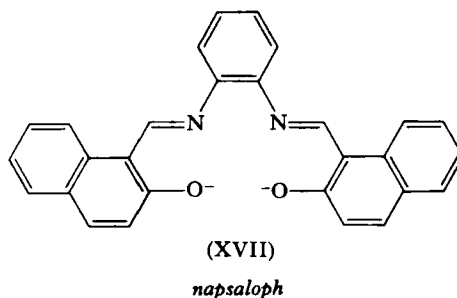
R = H *saloph*, *salophen*, *salphen*

R = Cl *4-Cl-saloph*, *saloph-Cl*



(XVI)

napsalen



II

COORDINATION CHEMISTRY

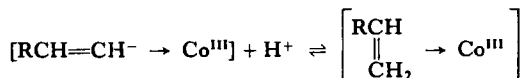
A. Valency and Spin State

The structures of organocobalt(III) complexes and the valency of the cobalt ion have been established by combinations of the usual techniques such as chemical analysis, measurements of magnetic susceptibility, IR and NMR spectroscopy, and chemical reactions to identify particular structural features, determinations of molecular weight and overall charge, X-ray diffraction, etc., though with interesting differences depending on the complexity of the compound in question. Thus, simple complexes such as $K_6[(NC)_5CoCH=CHCo(CN)_5]$ can be fully characterized by chemical analysis, IR and NMR spectra, and magnetic susceptibility (70). But in the case of the corrinoids, the first three techniques are useless. The major tool in characterizing 5-deoxyadenosylcobalamin (DBC) was X-ray diffraction (115, 114) together with measurements of magnetic susceptibility (86) and comparison of the structure of the conjugated corrin ring with that in cyanocobalamin by a set of chemical reactions involving methylcobalamin (87). The structures of all other organocorrinoids are simply assumed to be analogous to that of DBC because of similarities in the method of

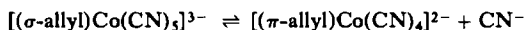
preparation, and in their chemical and physical properties [for examples see Chapters 7 and 13 of ref. (136)]. It is worth pointing out that organocobalt complexes are known in which the formal valency is Co(II), e.g., *trans*-[Co(PR₃)₂(aryl)₂] (31), or Co(I), e.g., CH₃Co(CO)₄ (81), and that 5-deoxyadenosylcobalamin was for some time considered to be a paramagnetic cobalt(II) complex [see discussion in ref. (85)].

All organocobalt(III) complexes, for which magnetic susceptibilities have been determined, are diamagnetic, whether six-coordinate, five-coordinate or dimeric (70, 86, 121, 49, 47, 38, 39, 64, 43, 174). The majority of the remaining complexes, including [(π -allyl)Co(CN)₄]²⁻ (109), have been studied by NMR spectroscopy and their spectra are consistent with the presence of a diamagnetic cobalt ion. But one cannot exclude the possibility that some particular combination of ligands may cause accidental degeneracy of, for example, the *d*_{z²} and *d*_{xy} orbitals and give rise to paramagnetism.

No organocobalt(III) complexes have yet been reported to contain a π -bonded olefin or acetylene, though the former probably occur as reaction intermediates (see Section VI,B,1,d). In other words, equilibria such as



lie far over to the left. The following type of equilibrium is, however, well established (see Section V,C).



We are therefore concerned almost exclusively with compounds which can be regarded as complexes of cobalt(III) with a coordinated carbanion (R⁻). It would be equally admissible to regard them as complexes of Co(II) containing a radical (R \cdot) with antiferromagnetic coupling of the spins, or of Co(I) with a carbonium ion (R⁺). In fact, in their reactions the transition state may correspond to any one of these three formulations. But since the ligands NC⁻, HC \equiv C⁻, CH₂=CH⁻, and CH₃CH₂⁻ form a regular, graded series in their effects on the chemical properties of the rest of the complex [see (139)], while alkyl ligands are similar to CN⁻ and NO₂⁻ in their effects on the *d-d* spectra (see Section II,D), it seems more sensible to treat them as cobalt(III) complexes. Calderazzo and co-workers also concluded from a comparison of the ⁵⁹Co NMR spectra of methyl- and acetyl-Co-salen with those of more conventional cobalt(III) complexes that the former should be considered as cobalt(III) complexes (64).

B. Stereochemistry

Three topics will be discussed here: (1) the configuration of the cobalt ion (octahedral, square-pyramidal, dimeric complexes), (2) details of the structure of the organo-ligand and its interaction with the equatorial ligand and (3) the existence of isomers. The most direct and unambiguous evidence on structural details comes, of course, from X-ray diffraction studies, but additional evidence is provided by the observation of chemical equilibria, NMR spectra, etc. The structures of 11 organocobalt(III) complexes have now been determined by X-ray analysis; some of the data relating to the immediate coordination sphere of the cobalt ion are given in Table 1.

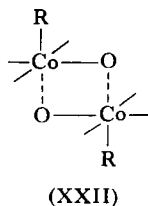
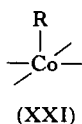
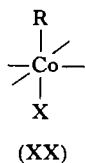
1. Configuration of the Cobalt Ion

The X-ray data show that organocobalt(III) complexes can exist in the three different stereochemical configurations shown diagrammatically in (XX)–(XXII).

(a) Six-coordinate, octahedral, as expected for most cobalt(III) complexes (XX).

(b) Five-coordinate, square-pyramidal (XXI).

(c) Dimeric, consisting of two square-pyramidal complexes, the second axial position of each cobalt being occupied by a coordinated atom (O in the case of salen) of the equatorial ligand of the other (XXII). In these dimers the relevant equatorial oxygen atoms use sp^2 -hybridized orbitals for forming the coordinate bonds within each half of the dimer, and pure p orbitals for forming the coordinate bonds linking the two halves. The latter bonds are expected to be much weaker.



The polymeric $[\text{NCCH}_2\text{Co}(\text{salen})]$ is a variant of the octahedral structure, in which the organo-ligand of one molecule also serves as the second axial ligand of the next in the polymeric chain. Solution studies have revealed other examples of five coordinated and dimeric complexes (see below).

In the case of BAE and salen complexes with simple alkyl ligands these different configurations can usually be distinguished by their color and

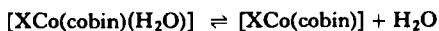
TABLE I: BOND LENGTHS AND ANGLES

R	L ₄	X	Co—C—C angle	Position of Co <i>vis-à-vis</i> L ₄ ligand atoms	Bond lengths (Å)			References
					Co—C	Co—L	Co—X	
<i>Six-coordinate, monomeric complexes</i>								
HCF ₂ CF ₂ —	(CN) ₄	CN	119.7°	—	1.990	1.894 (av.)	1.927	120
5-Deoxyadenosyl	corrin	Bzm ^a	125°	Approx. coplanar	2.05	1.92, 1.91, 1.97, 1.98	2.23	114
CH ₃ OOCCH ₂ —	(DMG) ₂	py	115°	Coplanar to with- in 0.02 Å	2.033	1.883, 1.891, 1.885, 1.896	2.043	112, 113
CH ₃ —	(DO)(DOH)pn	H ₂ O	—	Coplanar	1.99	1.86, 1.94, 1.92, 1.88	2.14	22
CH ₃ COCH ₂ —	salen	CH ₃ OH	Not given	Coplanar to with- in 0.05 Å	2.02	Not given	2.20	30
(NC) ₂ CH—	salpn-1,2	py	111°, 115°	—	2.02	Co—O, 1.88, 1.89; Co—N, 1.87, 1.90	2.07	4
CH ₂ =CH—	BAE	H ₂ O	127.2°	Coplanar	1.89	Co—O, 1.92; Co—N, 1.89	2.22	21
C ₆ H ₅ —	BAE	H ₂ O	—	—	1.93	Co—O, 1.91; Co—N, 1.89	2.33	24
<i>Six-coordinate, polymeric complexes</i>								
NCCH ₂ —	salen	NCCH ₂ Co	Not given	Coplanar to with- in 0.05 Å	1.99	Not given	2.09	30
<i>Five-coordinate complexes</i>								
CH ₃ —	BAE	—	—	0.12 Å above plane ^b	1.95	Co—O, 1.91; Co—N, 1.89	2.33	23
<i>Dimeric complexes</i>								
CH ₃ CH ₂ —	salen	O(salen) of other half	119.5°	0.06 Å above plane ^b	1.990	Co—O, 1.901, 1.935; Co—N, 1.886, 1.880	2.342	27

^a Bzm is 5,6-dimethylbenzimidazole. ^b Toward the C atom.

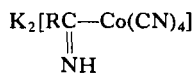
electronic spectra (see Section II,D). The octahedral complexes are orange, the five coordinate complexes green, and the dimers (at least in the case of methyl- and ethyl-Co(salen), which are the only two established so far) deep red. The five-coordinate complexes with ligands such as $\text{CH}_3\text{CO}-$ and $\text{CH}_2=\text{CH}-$ are, however, violet (40). In most cases the six-coordinate aquo complex is the product obtained from the reaction mixture in the absence of added bases such as pyridine or phosphines. The H_2O may be removed from the solid by drying over P_2O_5 or by gentle heating. The aquo complexes often dissolve in noncoordinating solvents such as CH_2Cl_2 to give green solutions, from which the five-coordinate solids can be obtained by recrystallization. Six-coordinate complexes containing other bases such as NH_3 or pyridine may in certain cases also be converted into their five-coordinate forms by heating. $\text{CH}_3\text{Co(salen)}$ is the only compound for which all three forms have been isolated in the solid state. The octahedral aquo complex can be dehydrated over P_2O_5 to give the green form, which is then converted slowly, if spontaneously, into the red dimer, rapidly if treated with anhydrous ether (64). The octahedral $[\text{EtCo(salen)}-\text{H}_2\text{O}]$ does not appear to exist and the dimer is obtained instead (47). For further examples of the existence of organocobalt complexes with the ligands BAE and salen in different configurations and for details of their preparation see Section IV and, in particular, refs. (64, 49, 47, 40, 43, 16, 17). Two studies have been carried out using NMR spectroscopy on the effect of the nature of the organo-ligand on the binding of ligands in the sixth position of BAE complexes. Formation constants for the binding of pyridine fell in the order $\text{R} = \text{vinyl} (K = 12 \text{ M}^{-1}) > \text{Me}(9) > \text{Ph}(6) > \text{Et}(1)$ (83). With a series of para-substituted phenyl ligands the formation constants for the binding of pyridine fell with the nature of the substituent in the order $\text{NO}_2 (K = 85 \pm 13 \text{ M}^{-1}) > \text{CN} > \text{Br} \sim \text{I} > \text{H} \sim \text{Me} \sim \text{MeO} (6.1 \pm 0.8)$; formation constants for the binding of piperidine showed a very similar variation (82).

Organo-corrinoids may also exist in both five- and six-coordinate forms; the presence of the corrin ring with its side chains prevents dimerization of the type found in $[\text{EtCo(salen)}]$. The two forms show marked differences in their electronic spectra and hence in their color; the six-coordinate forms are usually red, and five-coordinate yellow. Quantitative studies with aqueous solutions of the cobinamides show that the position of the following equilibrium is increasingly displaced to the right as the ligand X is changed



in the order (% five-coordinate form in H_2O at 20°C given in parentheses): CN^- (0), $\text{CH}_2=\text{CH}-$ (70), CH_3- (90), MeCH_2- and $\text{Me}_2\text{CH}-$ (both 100). This order of ligands is the same as that found for a variety of other cis and trans effects (see Section II,C). The following values were obtained for the changes in entropy and enthalpy involved in the loss of H_2O ; vinylcobinamide ΔH 4.5 ± 2.0 kcal/mole, ΔS 15.5 ± 7 e.u.; methylcobinamide ΔH 4.4 ± 2.0 kcal/mole, ΔS 16 ± 7 e.u. The reversible loss of H_2O to give the five-coordinate forms can also be brought about in the solid state merely by varying the partial pressure of water vapor (61). For further examples of equilibria involving five-coordinate organocobalt corrinoids see ref. (136, Section 8.3).

Organocobalt complexes with other equatorial ligands also show the ability to exist in more than one configuration. Both methyl- and acetyl-Co(saloph) can be obtained as anhydrous compounds and as the monohydrate, and five- and six-coordinate forms of the acetyl complex can be distinguished in solution by the frequency of the CO stretch (16). The complexes $[\text{RCo}(7\text{-Me-salen})]$ where R is Me, Et, CH_3CO , Ph, and CH_3OCO form red solids, but green solutions (16). Certain complexes of the type $[\text{RCo}(\text{DMG})_2\text{H}_2\text{O}]$ can be dehydrated by boiling the solutions in benzene; this reaction occurs readily with the methyl, sluggishly with the ethyl, and not at all with the propyl compound (161). It was shown later that the molecular weight of the methyl compound in CH_2Cl_2 corresponded to the dimer and that the NMR spectrum agreed with a dimeric structure formed by coordination of each cobalt atom to an oxygen atom of the other half (116a). Solutions of the complexes $[\text{RCo}(\text{CR})\text{Br}]^+\text{PF}_6^-$ in methanol gradually lose bromide ion to give the five-coordinate forms (131). Surprising color changes, whose cause is so far unknown, are found with $[\text{propylCo}(\text{phthal})]$; it forms, as expected, deep blue solutions in THF, DMF, and pyridine, but is ruby red in the solid state (174). There may even be cases of five-coordination among the organocyanide complexes; some of the products of decomposition of the ions $[\text{RCo}(\text{CN})_5]^{3-}$ in acid have a stoichiometry corresponding to five-coordination (101), e.g.,



Costa and co-workers have compared the effect of different equatorial ligands on the relative stability of the five- and six-coordinate forms by studying the tendency of the five-coordinate acetylcobalt complexes to bind

pyridine or *N*-methylimidazole in the sixth position, and report the following order of increasing stability of the six-coordinate forms: BAE < 7-Me-salen < salen < saloph \ll (DMG)₂ and (DO)(DOH)pn (16). No direct comparison has yet been made between these ligands and corrin.

2. Steric Features of the Organo-ligand

One of the surprising features revealed by the data in Table I is the large Co—C—C bond angle observed when the coordinated carbon atom is formally tetrahedral; in most cases the bond angle is closer to that of a trigonal (120°) than a tetrahedral (109.5°) carbon atom. This rehybridization of the carbon atom is presumably caused by the need to maximize the overlap with the relevant hybridized orbital of the cobalt and to minimize the various repulsions, in particular between the electron pairs in the C—C and C—H bonds on the one hand and the nonbonded electron pairs of cobalt (the *t*_{2g} subshell) and nitrogen on the other. It is interesting to see that in the octahedral complexes the cobalt ion lies within the plane formed by the four equatorial ligand atoms, but that in the five-coordinate complex the cobalt is displaced 0.12 Å above the plane towards the carbon atom of the single axial ligand. This obviously serves to reduce these repulsions and hence allows a shortening of the Co—C (tetrahedral) bond length from 1.99–2.05 Å in the six-coordinate complexes to 1.95 Å in the five-coordinate complex. The dimeric complex, in which the second axial ligand is bonded rather weakly represents an intermediate stage; the cobalt is displaced 0.06 Å above the plane of the equatorial ligand atoms towards the carbon atom. It would be interesting to see whether the Co—C—C bond angles are less abnormal in five-coordinate complexes.

Steric compression and repulsion involving the organo-ligand may also occur at points further removed from the cobalt. The increase in the C—Co—N(equatorial ligand) bond angle to 95° from the expected 90° in [MeOOCCH₂Co(DMG)₂py] is apparently due to contact between the carboxy carbon and a coordinated nitrogen atom of a DMG unit (112). The BAE ligand consists of two planar, conjugated halves, which are inclined at an angle to each other. In [PhCo(BAE)H₂O] the two halves are bent away from the phenyl ligand (at an angle of 8.9° to each other) and the Co—OH₂ is relatively long (2.33 Å) (24); while in [vinyl-Co(BAE)H₂O] the two halves are bent towards the vinyl ligand (at an angle of 11.2°) and the Co—OH₂ bond is much shorter (21). This presumably reflects the

greater steric hindrance of the phenyl compared to the vinyl group. The angle between the two halves is much smaller (4.0°) in the five-coordinate $[\text{MeCo}(\text{BAE})]$ (23). The salen ligand may also show considerable variation in conformation; in $[\text{CH}_3\text{COCH}_2\text{Co}(\text{salen})\text{MeOH}]$, for example, one half of the salen ligand is distorted by contact with the acetone moiety (30). The corrinoids show an even greater variation in the conformation of the equatorial ligand, though this is not due to contact with any organo-ligand. The corrin ring is nonplanar and buckled; examination of the structures of 5-deoxyadenosylcobalamin and other corrinoids shows the existence of four basic patterns of buckling (114).

A related phenomenon, apparently caused by interaction of the organo-ligand with the corrin ring and its substituents, is the absence of free rotation around the $\text{Co}-\text{C}$ bond revealed by the nonequivalence of the α and/or β -protons in the NMR spectra of *n*-propyl- and isopropylcobinamide and 5-deoxyadenosylcobalamin and cobinamide, though free rotation occurs in ethylcobinamide (88, 35, 20).

3. Geometrical and Optical Isomers

No cases of *cis/trans* isomerism have yet been reported among organocobalt(III) complexes, even among compounds not covered by this review. Complexes such as $[\text{R}_2\text{Co}(\text{bipy})_2]^+$ all have the *cis* configuration; steric hindrance would be greatly increased by the coplanarity of the two bipyridyl ligands in the *trans* isomer (123).

Isomers are, of course, possible when the equatorial ligand lacks a plane of symmetry, as in the corrinoids [see (III)]. All the acetamide side chains project to one side of the corrin ring, which we shall call the "upper" side, and all the propionamide side chains and the nucleotide side chain to the "lower" side. Isomers are then theoretically possible whenever the two axial ligands are different, and their existence has been shown experimentally for corrinoids where one axial ligand is CN^- , Me, or Et and the other is H_2O or is absent [for further details see Section 8.2 of ref. (136)]. Salen and BAE also show minor deviations from planarity due to the bending of the two halves (mentioned above in Section II,B,2) and to torsion about the $\text{C}-\text{C}$ bonds in the ethylene bridge (see references in Table I), but these are not expected to give rise to separable isomers.

Only one optically active simple organocobalt complex has so far been reported, namely $[\text{RCo}(\text{DMG})_2\text{py}]$, where R is the optically active 1-methylheptyl ligand (55). All cobalt corrinoids, where the ring has been

formed biosynthetically, are of course, optically active, and in addition the 5-deoxyadenosyl ligand (II) is optically active. Ligands such as salpn-1,2 contain an asymmetric carbon atom, but no attempt to separate any enantiomeric complexes has yet been reported; X-ray analysis of the structure of $[(\text{NC})_2\text{CHCo}(\text{salpn-1,2})\text{py}]$ shows disorder of the methyl groups in the propylene bridge (4).

C. *Cis and Trans Effects*

Changing one ligand in a complex can affect the physical and chemical properties of the other ligands; in the case of octahedral cobalt(III) complexes such a change can affect the ligands in both the *cis* and *trans* positions. Ligands can be arranged in an order of *cis* and *trans* effects depending on how they affect the other ligands in the complex. This is to be clearly distinguished from the order of ligands determined from their effect on the physical (i.e., spectroscopic and magnetic) properties of the central metal ion, i.e., the spectrochemical and nephelauxetic series; the *d-d* spectra of organocobalt(III) complexes are mentioned in Section II,D.

One of the most interesting aspects of the chemistry of cobalt(III) complexes is the existence of several series of complexes which differ only in one ligand (including organo-ligands), thus allowing a direct comparison of organo-ligands with the simpler, more "inorganic" ligands such as H_2O , NH_3 , Cl^- , or CN^- , usually studied by coordination chemists. Such comparisons have revealed the remarkably strong *cis* and *trans* effects exerted by alkyl and related ligands. Since recent reviews have covered the subject of *cis* and *trans* effects both in cobalt(III) complexes in general (139) and in cobalt(III) corrinoids in particular (136), only a very brief summary will be given here. The observed effects of a given ligand as compared with another can be divided into the following:

(1) Ground-state effects, i.e., the effects on the bond lengths and angles, stretching and bending force constants, and other spectroscopic properties of the other ligands.

(2) Thermodynamic effects, i.e., the effect on equilibrium constants for the substitution of one ligand by another (without a change in the coordination number), for the gain or loss of a ligand (with a change in the coordination number), or for some equilibrium involving another ligand which remains coordinated (e.g., gain or loss of a proton).

(3) Kinetic effects, i.e., the effect on the rates of the reactions listed under (2).

As a broad generalization, we can say that substitution of, say, H_2O , NH_3 or CN^- by CH_3^- leads to the following changes in complexes of the type discussed in this review: the other Co–ligand bond lengths increase, the properties of the other ligands approach those of the free ligands, the formation constants for the binding of all ligands in the sixth position fall, and the rates of gain, loss or substitution of ligands increase. As we have seen in Section II,B,1, the binding of the sixth ligand is often so weak that five-coordinate complexes may be obtained. For experimental evidence on the high rate of ligand substitution reactions in organocobalt(III) complexes see, for example, refs. (78) (corrinoids), (52, 143) (DMG complexes), (83) (BAE), and (48) ((DO)(DOH)pn).

D. *d–d Spectra*

The *d–d* transitions are most easily seen and identified in the pentacyanides $[\text{Co}(\text{CN})_5\text{X}]$. Compare the following wavelengths (in nm) of the first *d–d* transition (${}^1T_{1g} \leftarrow {}^1A_{1g}$): $\text{X} = \text{H}^-$, 305 (6); CN^- , 310 (73); $-\text{CF}_2\text{CF}_2\text{H}$, 311 (121); $-\text{CH}_3$, 318 (74); NH_3 , 345 (11); H_2O , 380 (73). This shows that both organo-ligands exert a very strong ligand field comparable with that of CN^- and establishes their position in the spectrochemical series. It is a pity that the second *d–d* transitions (${}^1T_{2g} \leftarrow {}^1A_{1g}$), which would establish the position of these ligands in the nephelauxetic series, have not yet been reported. Two bands have, however, been reported for the binuclear complex $[(\text{NC})_3\text{Co}(\text{CF}_2\text{CF}_2)\text{Co}(\text{CN})_5]^{6-}$ at 320 and 276 nm (121).

Costa and Busch and their co-workers have identified the three bands of lowest energy in organocobalt complexes of BAE, salen, $(\text{DMG})_2$, and CR as *d–d* transitions (47, 131). Calculations showed that the ligand field of the alkyl ligands was comparable to that of NO_2^- (i.e., between NH_3 and CN^-), and the relatively high extinction coefficients ($\sim 10^3$) were ascribed to a high degree of covalency in the metal–ligand bonds and to the absence of a center of symmetry (131).

III

FORMATION OF THE Co–C BOND

The Co–C bond can be formed by reactions of the following main types:

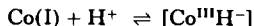
- Co(I) or Co–H complexes + electrophiles (e.g. CH_3I , $\text{HC}\equiv\text{CH}$, olefins)
- Co(II) complexes + radicals (and possibly electrophiles)
- Co(III) complexes + nucleophiles (e.g. RMgBr , CO)

In this section we concentrate on the types of reaction, their kinetics, stereochemistry, and mechanism, and deal with the above groups in turn; Section IV deals with the practical details of applying these and other reactions to the synthesis of organocobalt(III) complexes.

There are also two reactions of organo-Co(I) and Co(III) complexes which do not fit into the above groups. $[\text{CH}_3\text{Co}(\text{salen})\text{H}_2\text{O}]$ reacts with $\text{C}_3\text{F}_7\text{I}$ in ~ 3 days at room temperature or in 30 minutes on refluxing in ethylene glycol dimethyl ether to form $[\text{C}_3\text{F}_7\text{Co}(\text{salen})\text{H}_2\text{O}]$ (174a). Is this a simple electrophilic attack by the organic halide? Attempts to replace one alkyl ligand by another by, for example, treating $[\text{CH}_3\text{Co}(\text{DMG})_2\text{py}]$ with BuLi were, however, unsuccessful (161). Organo-Co(III) complexes of $(\text{DO})(\text{DOH})\text{pn}$, CR , and tim can be reduced to organo-Co(I) complexes, which can be further alkylated to give the *trans*-dialkyl-Co(III) complexes (60, 45, 42) (see also Section VI,E).

A. Reactions of Co(I) and Co—H Complexes

The simple Co(I) complexes may reversibly pick up a proton to give what is essentially a Co(III) complex with a coordinated hydride, i.e.,



These two types of complex may, and do, show differences in their behavior towards alkylating agents. The existence of this equilibrium was first demonstrated in the case of the pentacyanide complex, which exists as the hydride $[\text{Co}(\text{CN})_5\text{H}]^{3-}$ throughout the normal pH range (6), but loses a proton to form $[\text{Co}^{\text{I}}(\text{CN})_5]^{4-}$ in strongly alkaline solutions with a $\text{p}K$ of approximately 18–19 (76). A similar equilibrium has also been established for DMG and related complexes; the neutral $[\text{HCo}(\text{DMG})_2\text{PBu}_3]$ can, for example, be extracted from aqueous methanol into benzene or hexane, and phase distribution measurements suggested a $\text{p}K$ of 10.5 in 50% aqueous methanol (149). $[\text{Co}^{\text{I}}(\text{phthalTS})]$ is reversibly protonated in aqueous solution ($\text{p}K$ 6.6), and this has been ascribed to formation of the hydride complex (104). There is also some evidence that solutions of $[\text{Co}^{\text{I}}(\text{salen})]^-$ and $[\text{Co}^{\text{I}}(\text{BAE})]^-$ in THF are converted into the corresponding hydrides when treated with deaerated water (40, 43). By contrast, it has been shown that the corrinoids in aqueous solution remain square-planar, four coordinate, Co(I) complexes down to $\text{pH} \sim 5$, below which H_2 is rapidly evolved, perhaps via the formation of the hydride (136). Reversible

protonation is obviously a fairly general reaction of Co(I) complexes, though the pK depends strongly on the nature of the ligands. Examples of differences between the Co(I) and hydride complexes are given in the section below. An interesting example of the effect of solvent is the observation that among the DMG complexes both the Co(I) and hydride forms react with alkyl halides at similar rates in protic solvents, but that solutions of the hydride in dry hexane or benzene [the Co(I) complex is presumably not soluble in these solvents] are unreactive towards alkyl halides, ethylene oxides, ethyl acrylate, or acrylonitrile (149).

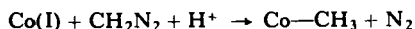
These complexes can react with a wide range of electrophilic reagents, which can be classified roughly into the following groups [equations are written only for Co(I) complexes].

(A) Substitution

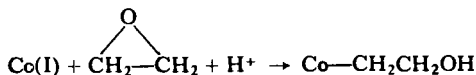
- (1) At a saturated carbon atom, i.e.,



where R may be alkyl, allyl, benzyl, fluoroalkyl, etc., and X^- may be Cl^- , Br^- , I^- , tosylate, carboxylate, $\frac{1}{2}\text{SO}_4^{2-}$, $\frac{1}{3}\text{PO}_4^{3-}$, R_3N , R_2S , Hg° , etc. Diazo-methane behaves similarly, i.e.,

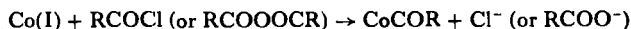


- (2) At a saturated carbon atom with ring-opening, e.g.,



Other examples are ethyleneimine, tetrahydrofuran, and β -lactones.

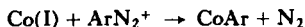
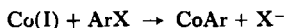
- (3) At an acyl carbon atom, e.g.,



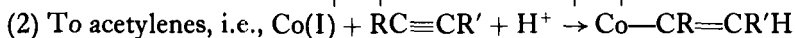
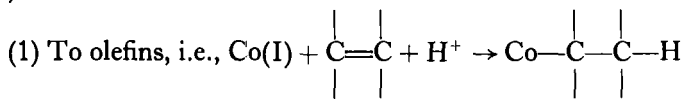
- (4) By an alkenyl halide, i.e., $\text{Co(I)} + \text{RCH=CHX} \rightarrow \text{CoCH=CHR} + \text{X}^-$

- (5) By an alkynyl halide, i.e., $\text{Co(I)} + \text{RC}\equiv\text{CX} \rightarrow \text{CoC}\equiv\text{CR} + \text{X}^-$

- (6) By an aryl halide or diazonium cation, i.e.,



(B) Addition



Depending on the various steric and electronic factors of both the alkylating agent and the cobalt complex, one may observe either (1) no reaction, (2) formation of an organocobalt complex, or (3) further reaction of the organocobalt complex, due to instability of the Co—C bond. Some examples of (1) and (3) are mentioned below. Reactions involving cleavage of the Co—C bond are discussed in more detail in Section VI,B. Information on the stereochemistry and mechanism is discussed separately for each type of reaction. Kinetic data have been reported only for A1. One complicating factor is that the Co(I) and hydride complexes may both react (but by different pathways) and it is sometimes not clear from the experimental data and reaction conditions which is the reactive complex.

A1, Alkyl Halides, etc. and A2, Epoxides, etc.

By studying the NMR spectra of the products, Jensen and co-workers were able to establish that the alkylation of (the presumed) $[\text{Co}^{\text{I}}(\text{DMG})_2\text{py}]^-$ in methanol by cyclohexene oxide and by various substituted cyclohexyl bromides and tosylates occurred primarily with inversion of configuration at carbon i.e., by an $\text{S}_{\text{N}}2$ mechanism. A small amount of a second isomer, which must have been formed by another minor pathway, was observed in one case (95). Both the alkylation of $[\text{Co}^{\text{I}}(\text{DMG})_2\text{py}]^-$ by asymmetric epoxides (129, 142) and the reduction of epoxides to alcohols by cobalt cyanide complexes (105, 103) show preferential formation of one isomer. In addition, the ratio of ketone to alcohol obtained in the reaction of epoxides with $[\text{Co}(\text{CN})_5\text{H}]^{3-}$ increases with pH and this has been ascribed to differing reactions with the hydride (reduction to alcohol) and Co(I) (isomerization to ketone) (103) (see also Section VII,C).

Schrauzer and co-workers have studied the kinetics of alkylation of Co(I) complexes by organic halides (RX) and have examined the effect of changing R, X, the equatorial, and axial ligands (148, 147). Some of their rate constants are given in Table II. They show that the rates vary with X in the order $\text{Cl} < \text{Br} < \text{I}$ and with R in the order methyl > other primary alkyls > secondary alkyls. Moreover, the rate can be enhanced by substituents such as Ph, CN, and OMe. *tert*-Butyl chloride will also react slowly with $[\text{Co}^{\text{I}}(\text{DMG})_2\text{py}]^-$ to give isobutylene and the Co(II) complex, presumably via the intermediate formation of the unstable *tert*-butyl complex. In the case of Co(I) cobalamin, the Co(II) complex is formed in the reaction with isopropyl iodide as well as *tert*-butyl chloride. Solvent has only a slight effect on the rate, e.g., the rate of reaction of Co(I) cobalamin

TABLE II
 RATES OF ALKYLATION OF Co(I) COMPLEXES BY
 ORGANIC HALIDES^a
 $\text{Co(I)}^- + \text{RX} \rightarrow \text{R-Co} + \text{X}^-$

R	$K_2 \text{ (M}^{-1} \text{ sec}^{-1}\text{)}$		I
	X = Cl	Br	
	(1) $[\text{Co}^{\text{I}}(\text{DMG})_2\text{PBU}_3]^-$		
Me	8.5×10^{-1}	2.2×10^2	2.3×10^3
Et	9.0×10^{-3}	1.6	—
<i>n</i> -Pr	6.3×10^{-3}	1.5	—
<i>i</i> -Pr	3.2×10^{-4}	1.1×10^{-1}	3.2
PhCH ₂ —	4.4×10^2	1.9×10^4	—
NCCH ₂ —	1.6×10^3	—	—
MeOCH ₂ —	$>1 \times 10^4$	—	—
	(2) $[\text{Co}^{\text{I}}\text{Cobal}]^-$		
Me	5.0	1.6×10^3	3.4×10^4
Et	4.7×10^{-2}	3.1×10^1	—
<i>n</i> -Pr	3.7×10^{-2}	1.4×10^1	—
<i>i</i> -Pr	—	1.8	2.3×10^2

^a Conditions: 0.1 *F* NaOH in methanol, 25°C. From ref. (147).

with CH₃Cl is 6.2 times faster in water than in methanol (147). The addition of a base has no significant effect on the rate of reaction with Co(I) cobalamin (as expected, since it does not appear to coordinate bases), but with other Co(I) complexes it decreases the rates of alkylation in the approximate order (for the same concentration of base) no base > py > Me₂S > PBU₃ > cyclohexyl isocyanide. Since the formation constants of the adducts were not determined, these results are only qualitative (147). A general comparison of the rates of alkylation with various RX and B suggested that the rates fell with the nature of the equatorial ligand in the approximate order: ? salen, ? porphyrin > corrin > (DMG)₂ > (CHD)₂ > (CPD)₂ ≥ (DPG)₂ > (DO)(DOH)en ~ (DO)(DOH)pn > (DMG-BF₂)₂ (147). A variety of observations suggest that BAE may have an even greater effect than salen (16), since it is the only Co(I) complex reported to react with a simple aryl halide (see A6). But the most interesting comparison is, perhaps, with other nucleophiles, using the nucleophilic reactivity constant ($n_{\text{CH}_3\text{I}}$), which is defined as $n_{\text{CH}_3\text{I}} = \log(K_Y/K_{\text{CH}_3\text{OH}})$ where K_Y and $K_{\text{CH}_3\text{OH}}$ are the second-order rate constants for the reactions of CH₃I in methanol at 25°C with

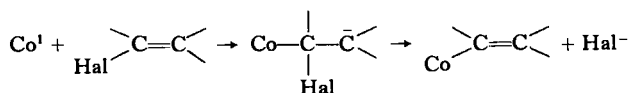
the nucleophile Y and with methanol (i.e., solvolysis), respectively. Schrauzer *et al.* quote the following values for Co(I) complexes and certain other nucleophiles: CH₃OH, 0.00; Cl⁻, 4.37; NH₃, 5.50; Br⁻, 5.79; I⁻, 7.42; PBu₃, 8.69; S₂O₃²⁻, 8.95; Ph₃Sn⁻, 11.5; Ph₃Ge⁻, 12; [Co^I(DMG)₂X]⁻ where X = PBu₃ 13.3, py 13.8, and H₂O 14.3; [Co^Icobal], 14.4 (148). Co(I) salen, porphyrin, and BAE probably have even higher values (see above). It is clear that Co(I) complexes are some of the most active nucleophiles known. The hydrido-Co(DMG)₂ complexes apparently react with alkyl halides in protic solvents at rates similar to those of the Co(I) complexes, but no experimental details or results have been given (149).

A3, Acyl Halides, etc.

No mechanism or kinetic data reported.

A4, Alkenyl Halides

Duong and Gaudemer studied the alkylation of (presumably) [Co^I(DMG)₂X]⁻, where X is pyridine, aniline, or water, by the *cis* and *trans* isomers of β -bromostyrene (PhCH=CHBr) and the methyl ester of β -chloroacrylic acid (CHCl=CHCOOMe) in 50% aqueous methanol, and found that the configuration of the double bond remained unchanged, i.e., the halogen had simply been replaced by cobalt. They suggested that the reaction involved the addition of cobalt, followed by the elimination of the halide ion (apparently without rotation around the C—C bond), i.e.,



Change of base (pyridine, aniline, water) had no obvious effect on the steric course of the reaction (59). Rather surprisingly, it appears that the reactions of the *cis* and *trans* isomers of 1-bromopropene with the hydride [Co(CN)₅H]³⁻ give different products; this eliminates an initial addition of Co—H to the double bond, since this would lead to the same product for the two isomers (105). Vinyl chloride apparently reacts only with [Co^Isalen]⁻, and not with the hydride, to form the CH₂=CHCo complex (43); the same may be the case with the BAE complexes (40).

A5, Alkynyl Halides

The only reported example appears to be the reaction of bromoacetylene (BrC≡CH) with Co(I) cobalamin, which gives both HC≡CCo (by

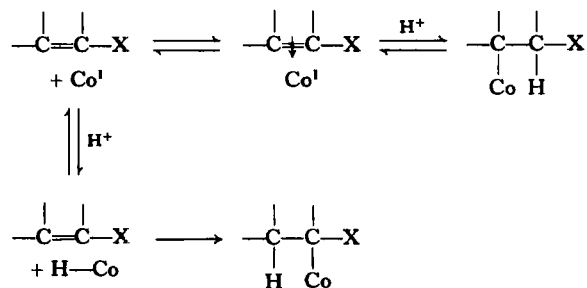
substitution) and $\text{BrCH}=\text{CHCo}$ (by addition) (97); there is no evidence to suggest whether the two products are due to different reactions with the Co(I) and Co-H complexes.

A6, Aryl Halides, etc.

The only reported reaction of a simple aryl halide is that of bromobenzene with $[\text{Co}^{\text{I}}(\text{BAE})]^-$, which appears to be one of the most nucleophilic Co(I) complexes (46, 16). α -Iodopyridine also reacts with $[\text{Co}(\text{CN})_3\text{H}]^{3-}$ (75).

B1, Addition to Olefins

Some interesting differences are found between the reactions of Co(I) and Co-H complexes. For example, $[\text{Co}^{\text{I}}(\text{DMG})_2\text{py}]^-$ will react at pH 10–11 with activated olefins to give the β -substituted complexes $[\text{XCH}_2\text{CH}_2\text{Co}(\text{DMG})_2\text{py}]$, where X is COOH , COOR , CN , etc.; but at pH 7–8, where the complex is present as the hydride, the α -substituted derivatives $[\text{CH}_3\text{CHXCo}(\text{DMG})_2\text{py}]$ are formed (163, 149). Schrauzer, Weber, and Beckham were able to show that the reactions at higher pH proceeded via the intermediate formation of the π -olefin- Co(I) complex (159). The reactions involving Co(I) appear generally to be reversible and the addition of Co-H irreversible (see also Section V,C and VI,B). We can, therefore, write the scheme



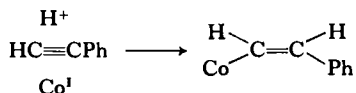
The observed isomerization of β - to α -substituted complexes probably occurs via this reaction sequence (163, 159). However, change of pH does not always change the nature of the product, e.g., styrene gives the α -phenylethyl complex $(\text{CH}_3\text{CHPhCo})$ at all pH's (163). In certain other cases one complex may react further or not at all, e.g., crotononitrile gives the α -substituted complex in neutral solution, but is reduced to butyronitrile in alkaline solution, while methylacrylonitrile gives the α -substituted

complex in neutral solution, but apparently does not react in alkaline solution (163). $[\text{Co}(\text{CN})_5\text{H}]^{3-}$ appears to react similarly to the above-mentioned hydride; acrylate and *trans*-crotonate give the α -substituted products ($\text{RCH}_2\text{CH}(\text{COOH})\text{Co}$), where $\text{R} = \text{H}$ and CH_3 (94). 2-vinylpyridine gives the α -(2-pyridyl)ethyl complex (102), and experiments with $[\text{Co}(\text{CN})_5\text{D}]^{3-}$ also suggest that D adds to the β -carbon (and hence Co to the α) in styrene, α -methylstyrene, α -vinylpyridine, methyl methacrylate and cinnamate (105). However, $[\text{NCCCH}_2\text{CH}_2\text{Co}(\text{salen})\text{H}_2\text{O}]$ is apparently formed by the reaction of $\text{CH}_2=\text{CHCN}$ with the hydride, not the Co(I) complex (43).

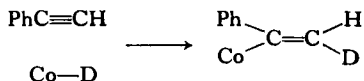
Jackman, Hamilton, and Lawlor have studied the stereochemistry of the addition of $[\text{Co}(\text{CN})_5\text{D}]^{3-}$ to α,β -unsaturated acids and identified the product of the addition of fumarate as the *threo* isomer, i.e., adduct formation has occurred by a stereospecific *cis* addition of $\text{Co}-\text{D}$ across the double bond (94).

B2, Addition to Acetylenes

Naumberg, Duong, and Gaudemer (129) have studied the stereochemistry of the addition of various acetylenes to $[\text{Co}^{\text{I}}(\text{DMG})_2\text{py}]^-$ in methanol. They found, as already noted by Schrauzer and Windgassen (163), that the main product from the reaction with phenylacetylene in alkaline solution ($\text{pH} \geq 10.5$) was the β -phenylvinyl complex ($\text{PhCH}=\text{CHCo}$), formed by the *trans* addition of the Co(I) anion and a proton, i.e.,



But in neutral solution, where the complex is present mainly as the hydride, the only product was the α -phenylvinyl complex ($\text{CH}_2=\text{CHPhCo}$). When the Co(I) complex was formed by reduction with D_2 or NaBD_4 in CH_3OH the reaction in neutral solution gave a product containing a significant amount of deuterium in the position *cis* to cobalt. This establishes the mechanism as the stereospecific *cis* addition of $\text{Co}-\text{D}$ across the double bond, i.e.,

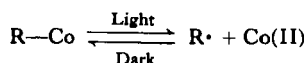


Phenylacetylene is apparently one of the few acetylenes so far reported which is able to react via the *cis* addition of $\text{Co}-\text{H}$. Methyl propiolate, ethyl

tetrolate, acetylenedicarboxylic acid dimethyl ester, and 3,3,3-trifluoroprop-1-yne all react via the trans addition of Co and H, even in neutral solution (129), though propargyl alcohol can give both cis and trans products (59). The α -phenylvinyl complex is also formed by the reaction of phenylacetylene with the hydride $[\text{Co}(\text{CN})_5\text{H}]^{3-}$ (105). Moreover, the homogeneous hydrogenation of phenylethynecarboxylic acid ($\text{PhC}\equiv\text{CCOOH}$), catalyzed by cobalt cyanide complexes, gives *cis*-cinnamic acid ($\text{PhCH}=\text{CHCOOH}$) as the major initial product (10). For the addition of bromoacetylene to Co(I)-cobalamin see A5, above.

B. Reactions of Co(II) Complexes

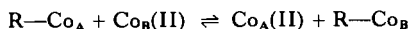
Co(II) complexes react rapidly with free radicals but, because of the difficulty of handling radicals, most of the evidence is indirect. The radicals and Co(II) complexes can both be prepared *in situ* by photolysis of organocobalt(III) complexes, i.e.,



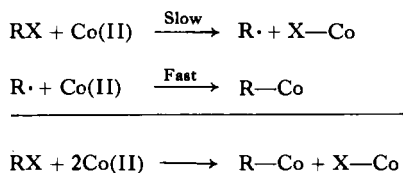
The reversibility of this reaction has been demonstrated in the case of methylcobalamin (140), and the same probably applies to most other organocobalt(III) complexes (see Section VI,A). Evidence for analogous and reversible thermal dissociation comes from the fact that the isomeric forms of methylcorrinoids, which differ in the relative orientation of the axial ligands, may be interconverted either by heating at $\sim 90^\circ\text{C}$ or by irradiating at room temperature, both in an inert atmosphere [see, for example, ref. (66) and Section 8.2.3 of ref. (136)]. Transfer of the methyl group from one complex to another occurs on irradiating a solution containing a methyl-Co(DMG)₂ complex and Co(II) cobalamin (158), and labeling experiments show that methyl groups are exchanged on heating a solution of methylcobalamin and methylcobinamide at 95°C (65).

A rapid, nonphotochemical, transfer of the alkyl group has been observed at 44°C between $[\text{MeCo}(\text{BAE})\text{H}_2\text{O}]$ and $[\text{Co}^{\text{II}}(\text{tfen})]$ in both the forward and reverse directions, and from the ethyl, but not the pentafluoroethyl, analog; and it was suggested that the reaction involved electron transfer accompanied by the transfer of the alkyl group (174a). Whatever the best description of the mechanism, it presumably involves direct transfer

between two cobalt ions, and not the intermediate formation of free radicals, i.e.,

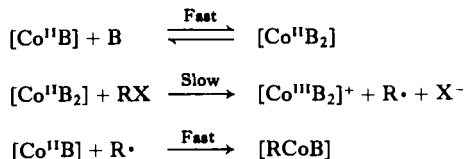


Free radicals can also be formed *in situ* by the abstraction of a halogen atom from an organic halide (RX) as in the sequence of reactions:

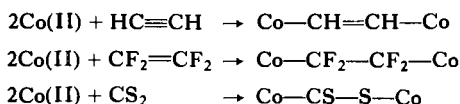


This mechanism was first proposed by Kwiatak and Seyler (109) for reactions with $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$, and the kinetics have been studied by Halpern and co-workers in water or aqueous methanol using a wide range of mono- and dihalides (75, 32). This mechanism is supported by the facts that the products are often (e.g., when R = methyl, benzyl, $-\text{CH}_2\text{COOH}$) approximately equimolar mixtures of the organo- and halopentacyanides, the reactions are first order in both cobalt and RX, the rate shows an inverse dependence on the C—X bond energy (i.e., $\text{RCl} < \text{RBr} < \text{RI}$, $\text{X—CH}_2\text{R} < \text{X—CHR}_2$ and $\text{ClCH}_2\text{R} < \text{Cl}_2\text{CHR} < \text{Cl}_3\text{CR}$) (32, 75), and the intermediate formation of free radicals can be deduced from their dimerization products (e.g., dibenzyl from benzyl halides) (109) or by trapping (e.g., with acrylonitrile) (109, 108). In many cases the free radicals and organopentacyanides may undergo other reactions; see, for example, refs. (32, 105). A similar mechanism was proposed on the basis of kinetic studies for the reaction of benzyl halides with five-coordinate complexes of the type $[\text{Co}^{\text{II}}\text{L}_4\text{B}]$, where L_4 is $(\text{DMG})_2$, $(\text{DPG})_2$, $(\text{DMPG})_2$, $(\text{DNPG})_2$, or saloph, and B an amine or phosphine, in benzene, acetone or methylene chloride (144, 119); it was also mentioned in a footnote that salen complexes resembled saloph complexes (119). It was found that variation of B could change the rate (of halogen abstraction) by a factor of $\sim 10^3$; the rate increased with increasing basicity among the amines, but no simple pattern was found for the phosphines. On the other hand, comparison of rates with the same B, RX, and solvent showed that varying the equatorial glyoxime ligand had little effect; unfortunately, no direct comparison can be made with the saloph and pentacyanide complexes. It is interesting that the reaction of *p*-nitrobenzyl

bromide in CH_2Cl_2 with the six-coordinate $[\text{Co}^{\text{II}}(\text{salen})(1\text{-methylimidazole})_2]$ proceeds by a different mechanism, which involves an initial electron transfer (118), i.e.,



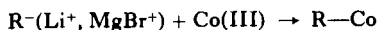
Dinuclear complexes can be formed by the reaction of C_2H_2 with $[\text{Co}^{\text{II}}(\text{CN})_3]^{3-}$ (70) and $[\text{Co}^{\text{II}}(\text{DMG})_2\text{X}]$, where $\text{X} = \text{H}_2\text{O}$ or pyridine, (163), C_2F_4 with $[\text{Co}^{\text{II}}(\text{CN})_3]^{3-}$ (121) and CS_2 with $[\text{Co}^{\text{II}}(\text{CN})_3]^{3-}$ (5, 125) according to the following schemes:



But no mechanistic studies have been carried out and participation by a $\text{Co}(\text{I})$ or CoH complex, formed by disproportionation, cannot be ruled out.

C. Reactions of $\text{Co}(\text{III})$ Complexes

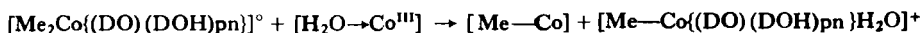
Reactions with powerful nucleophiles such as Grignard reagents can only be applied to complexes which are soluble in organic solvents which do not decompose the alkylating agent. This method was first used in the organocobalt field by Wagner and Bernhauer in 1964 (176), who used both Grignard reagents and lithium alkyls to alkylate $\text{Co}(\text{III})$ corrinoids possessing esterified side chains. It has subsequently been applied to many other types of complex (see Table III). These reactions can be written schematically:



Brief mention has been made of the use of Li, Na, B, and Al alkyls to form organocobalt-DMG complexes, but no details have been given except that tri-*n*-butylboron will react with either the dimeric $[\text{Co}^{\text{II}}(\text{DMG})_2\text{py}]$ or $[\text{Co}^{\text{III}}(\text{DMG})_2\text{pyCl}]$ to give $[\text{BuCo}(\text{DMG})_2\text{py}]$ and that the yield is greater with the former (161); it is difficult to know what the mechanism is.

Costa and co-workers recently extended the scope of this type of reaction to alcoholic and aqueous solutions by showing that certain compounds such as nitromethane (CH_3NO_2) and acetone (CH_3COCH_3), which contain an active (i.e., ionizable) hydrogen, will react readily with the aquohydroxo-Co(III) complexes of salen, 7-Me-salen and saloph to give complexes containing the ligands CoCH_2NO_2 and $\text{CoCH}_2\text{COCH}_3$ (16). Complexes of salen and salpn-1,2 containing the ligand $\text{CoCH}(\text{CN})_2$ have also been prepared by the reaction of malononitrile (NCCH_2CN) with the Co(III)-methoxide complex in aqueous methanol (4). These reactions presumably proceed via reaction of the free carbanion with the Co(III) complex.

Costa and co-workers have also shown that the Co—C bond may be formed by transfer reactions of the type



(for further details see Section VI,C,1,b) and by the insertion of CO. Costa, Mestroni, and Pellizer (44) found that CO will react with methanolic solutions of methoxide complexes (usually prepared by treating a solution of a halide complex with NaOCH_3) of salen, BAE, and $(\text{DMG})_2$ to give the alkoxycarbonyl complex in quantitative yield, i.e.,



Since acidification liberates CO and the alcohol (45), the reaction is essentially reversible. The reaction presumably occurs via the substitution [usually a $\text{S}_{\text{N}}1$ reaction (139)] of the coordinated alkoxide by CO, which then adds the alkoxide. In an extension of this reaction, the photolysis of solutions of $[\text{RCo}(\text{salen})\text{H}_2\text{O}]$ ($\text{R} = \text{Me}, \text{Et}, n\text{-Pr}, n\text{-Bu}$) in alcohols $\text{R}'\text{OH}$ ($\text{R}' = \text{Me}, \text{Et}, i\text{-Pr}$) in the presence of oxygen yields the complexes $[\text{R}'\text{OCOCO}(\text{salen})\text{-H}_2\text{O}]$, in which the alkoxy group is derived from the solvent (37, 44).

IV

PREPARATIVE METHODS

In this section, the corrinoids, the other macrocyclic complexes, and the cyanides are dealt with separately (Sections A–C). The preparative organometallic chemist will be primarily interested in Sections B and C, whereas

the inorganic chemist interested in biochemistry will want to refer primarily to Section A. [For a more complete account see the recent book, ref. (136).] The divisions have been made so that specialists in each area may follow progress in their own fields without necessarily having to read through sections which are not of direct interest to them. The general classification of preparative methods is the same as that made for the mechanistic discussions in Section III, viz. (1) Co(I) and electrophiles, (2) reactions involving Co(II), and (3) Co(III) and nucleophiles. The last route has so far not been applied to pentacyanides. The detailed arrangement within each section is slightly different from that in Section III, however, because it is made to reflect experimental method rather than mechanistic type. The nomenclature used in the summary in Table III is based on the classification of preparative methods used in the present section.

The experimental details are mentioned as they arise; often air must be excluded from the reactions but there are many examples when this exclusion is not important (or may even be fatal!) to the reaction. A general point is that nearly all of these organocobalt(III) complexes are unstable to visible light, and so light should be excluded during the preparations at all times whenever the organocobalt(III) complex is in solution. The solid complexes are stable to visible light.

Details of complexes which have been prepared are given in Table III, 1-29.

TABLE III

THE PREPARATION AND CHARACTERIZATION OF ORGANOCOBALT(III) COMPLEXES OF THE GENERAL FORMULA $[\text{RCo}^{\text{III}}(\text{L}_4)\text{X}]$ where L_4 is the equatorial ligand (Corrin, etc.) and X is the unidentate axial ligand (5,6-dimethylbenzimidazole, H_2O or absent, where L_4 is corrin; otherwise as stated in the table).

The following classification and abbreviations are used in the Table.

Methods of preparation (for details see Sections III and IV)

1. Reactions involving Co(I)
 - 1A. Substitution
 - 1B. Addition
2. Reactions involving Co(II)
 - 2A. Radicals and Co(II)
 - 2B. Electron transfer
3. Reactions involving Co(III)
 - 3A. Nucleophilic attack on Co(III)
 - 3B. $[\text{RO}-\text{Co}(\text{L}_4)\text{X}]$ with active hydrogen compounds

TABLE III *continued*

4. From other organocobalt(III) compounds
 4A. Reactions involving the axial ligand
 4B. Reactions involving the organic ligand
 4C. Reactions involving the equatorial ligand
 4D. Reactions of $[R-Co(L_4)X]$ with CO, O₂, and R'OH.

Methods of characterization

- a Infrared spectra
- b Nuclear magnetic resonance spectra
- c UV-visible spectra
- d Elemental analysis

Ligands

THF, tetrahydrofuran; DMF, dimethylformamide; DMSO, dimethyl sulfoxide; DPSO, diphenyl sulfoxide; en, ethylenediamine; py, pyridine; pic, picoline; lut, lutidine; nic, nicotinamide; IMD, imidazole; MeIMD, *N*-methylimidazole; 1-Cl-nap, 1-chloronaphthyl; acac, acetylacetonate anion, $CH_3COCHCOCH_3$; $C_6H_5O_3$, acetoacetic ester anion, $CH_3COCHCOOC_2H_5$; $C_4H_{10}N_2$, piperazine; $C_7H_5N_2$, benzimidazole.

Where the second axial ligand or counter-anion is not known (e.g., in solution), this is indicated by ?. Dinuclear complexes are indicated by the addition of two Co atoms to the formula of the ligand, e.g., $Co-CH=CH-Co$.

1. L_4 = corrin

R	Prep. and characterization ^a
CH ₃ to <i>n</i> -C ₁₀ H ₂₁ , incl.	1A, c [2A, 3A for R = CH ₃ , b for R = CH ₃ , and C ₂ H ₅]
<i>i</i> -C ₃ H ₇	1A, c
CH ₃ CH ₂ CH(CH ₃)	1A, c
cyclo-C ₆ H ₁₁	1A, c
C ₆ H ₅ CH ₂	1A, c
CH ₂ =CH	1A, 1B, b, c
CH ₂ =CHCH ₂	1A, c
HC≡C	1A, c
CoCH ₂ (CH ₂) ₂ CH ₂ Co	1A, 4B, c
HOCH ₂ CH ₂	1A, c
HOCH ₂ (CH ₂) ₂ CH ₂	1A, c
CH ₃ CH(OH)CH ₂	1A, c
HOCH ₂ CH(OH)CH ₂	1A, c
BrCH ₂ (CH ₂) ₂ CH ₂	1A, c
ClCH ₂	1A, c
Cl ₂ CH	1A, c
Br ₂ CH	1A, c
Cl ₃ C	1A, c
F ₂ ClC	1A, c
CF ₃ CH ₂	1A, c
BrCH=CH	1A, 1B, c
HCF ₂ CF ₂	1B, c
NCCH ₂ CH ₂	1A, c

TABLE III *continued*1. L_4 = corrin

R	Prep. and characterization ^a
NH ₂ CH ₂ CH ₂	1A, c
HOOCCH ₂	1A, c
HOOCCH ₂ CH ₂	1A, 1B, c
HOOCCH=CH	1B, c
CH ₃ OOCCCH ₂	1A, c
CH ₃ OOCH ₂ CH ₂	1A, c
HSO ₃ CH ₂	1A, c
CH ₃ CO	1A, c
C ₂ H ₅ OCO	1A, c
RNHCH ₂ CO	1A, c
5-Deoxyadenosyl	1A, c

^a For a more complete list, and for original sources see ref. (136).2. L_4 = porph

R	X	Prep. and characterization	References
CH ₃	H ₂ O	1A, 3A, b, c, d	33, 56
C ₂ H ₅	H ₂ O	1A, 3A, b, c, d	33, 56
<i>n</i> -C ₃ H ₇	H ₂ O	3A, b, c, d	33
<i>n</i> -C ₄ H ₉	H ₂ O	3A, b, c, d	33
CH ₂ =CHCH ₂	H ₂ O	3A	56
cyclo-C ₆ H ₁₁	H ₂ O	3A	56
HOCH ₂ CH ₂	H ₂ O	1A, b, c, d	33, 34
HOCH ₂ CH ₂ CH ₂	H ₂ O	1A, b, c, d	33, 34
CH ₃ CO	H ₂ O	1A, a, b, c, d	33
C ₆ H ₅	H ₂ O	3A, c, d	33, 56
<i>m</i> -CH ₃ C ₆ H ₄	H ₂ O	3A, b, c, d,	33
<i>p</i> -CH ₃ C ₆ H ₄	H ₂ O	3A, b, c, d	33

3. L_4 = phthal

R	X	Prep. and characterization	References
CH ₃	H ₂ O	1A, c	54
CH ₃	CN ⁻	4A, c	54
C ₂ H ₅	—	1A	54
<i>n</i> -C ₃ H ₇	THF	1A	174
<i>n</i> -C ₄ H ₉	—	1A	54

TABLE III *continued*4. $L_4 = \text{phthalTS}$

R	X	Prep. and characterization	References
CH ₃	—	1A, b, c	54

5. $L_4 = \text{CR}$

R	X	Anion	Prep. and characterization	References
CH ₃	—	PF ₆ ⁻ and Br ⁻	4A, c	131
CH ₃	H ₂ O	PF ₆ ⁻ and Br ⁻	4A, c	131
CH ₃	py	PF ₆ ⁻ and Br ⁻	4A, c	131
CH ₃	(C ₆ H ₅) ₃ P	PF ₆ ⁻ and Br ⁻	4A, c	131
CH ₃	Br ⁻	PF ₆ ⁻	1A, b, c, d	130, 131
CH ₃	CH ₃ ⁻	(C ₆ H ₅) ₄ B ⁻	4A, b	60
CH ₃	C ₆ H ₅ CH ₂ ⁻	(C ₆ H ₅) ₄ B ⁻	4A	60
C ₂ H ₅	—	PF ₆ ⁻ and Br ⁻	4A, c	131
C ₂ H ₅	H ₂ O	PF ₆ ⁻ and Br ⁻	4A, c	131
C ₂ H ₅	Br ⁻	PF ₆ ⁻	1A, b, c, d	130, 131
<i>n</i> -C ₄ H ₉	H ₂ O	PF ₆ ⁻ and Br ⁻	4A, c	131
<i>n</i> -C ₄ H ₉	Br ⁻	PF ₆ ⁻	1A, b	131
CH ₂ =CHCH ₂	Br ⁻	PF ₆ ⁻	1A	130, 131
CH ₂ =CH	Br ⁻	PF ₆ ⁻	1A, a, d	130, 131
ClCH ₂	Br ⁻	PF ₆ ⁻	1A, c, d	130, 131
NCCH ₂ CH ₂	Br ⁻	PF ₆ ⁻	1A, a, d	130, 131
C ₆ H ₅ CH ₂	H ₂ O	PF ₆ ⁻ and Br ⁻	4A, c	131
C ₆ H ₅ CH ₂	Br ⁻	PF ₆ ⁻	1A, c, d	130, 131

6. $L_4 = \text{tim}$

R	X	Anion	Prep. and characterization	References
CH ₃	Br ⁻	(C ₆ H ₅) ₄ B ⁻	1A, b	60
CH ₃	CH ₃ ⁻	(C ₆ H ₅) ₄ B ⁻	4A	60
CH ₃	C ₆ H ₅ CH ₂ ⁻	(C ₆ H ₅) ₄ B ⁻	4A	60

7. $L_4 = (\text{DO})(\text{DOH})\text{en}$

R	X	Anion	Prep. and characterization	References
CH ₃	H ₂ O	(C ₆ H ₅) ₄ B ⁻	1A, d	158
CH ₃	H ₂ O	ClO ₄ ⁻		117a
C ₂ H ₅	H ₂ O	(C ₆ H ₅) ₄ B ⁻	1A, d	158

TABLE III *continued*7. $L_4 = (\text{DO})(\text{DOH})\text{en}$

R	X	Anion	Prep. and characterization	References
$n\text{-C}_3\text{H}_7$	—	?	1A	147
$n\text{-C}_3\text{H}_7$	py	?	1A	147
$n\text{-C}_3\text{H}_7$	$(n\text{-C}_4\text{H}_9)_3\text{P}$?	1A	147
$n\text{-C}_3\text{H}_7$	$(\text{CH}_3)_2\text{S}$?	1A	147

8. $L_4 = (\text{DO})(\text{DOH})\text{pn}$

R	X	Anion	Prep. and characterization	References
CH_3	H_2O	ClO_4^-	1A, 3A, d	39, 46, 158
CH_3	H_2O	$(\text{C}_6\text{H}_5)_4\text{B}^-$	1A, 3A, d	39, 46
CH_3	H_2O	I^-		42
CH_3	IMD	$(\text{C}_6\text{H}_5)_4\text{B}^-$	1A, d	46
CH_3	IMD	PF_6^-	1A, d	46
CH_3	MeIMD	ClO_4^-	1A, d	46
CH_3	$\text{C}_7\text{H}_6\text{N}_2$	ClO_4^-	4A, d	46
CH_3	NH_3	$(\text{C}_6\text{H}_5)_4\text{B}^-$	4A, d	46
CH_3	DMF	?		50
CH_3	$(\text{C}_6\text{H}_5)_3\text{P}$?	4A	48
CH_3	SCN^-	—	4A, d	46
CH_3	I^-	—	4A, d	39, 42, 46
CH_3	CH_3^-	—	1A, 3A, 4A, d	42, 45
C_2H_5	H_2O	ClO_4^-	1A, 3A, d	39, 46, 158
C_2H_5	H_2O	$(\text{C}_6\text{H}_5)_4\text{B}^-$	1A, 3A, d	39, 46
C_2H_5	IMD	$(\text{C}_6\text{H}_5)_4\text{B}^-$	1A, d	46
C_2H_5	IMD	PF_6^-	1A, d	46
C_2H_5	MeIMD	ClO_4^-	1A, d	46
C_2H_5	$\text{C}_7\text{H}_6\text{N}_2$?	4A	48
C_2H_5	DMF	?		50
C_2H_5	$(\text{C}_6\text{H}_5)_3\text{P}$?	4A	48
C_2H_5	I^-	—		39
$n\text{-C}_3\text{H}_7$	H_2O	ClO_4^-	1A, 3A, d	46, 147, 158
$n\text{-C}_3\text{H}_7$	IMD	$(\text{C}_6\text{H}_5)_4\text{B}^-$	1A, d	46
$n\text{-C}_3\text{H}_7$	$\text{C}_7\text{H}_6\text{N}_2$?	4A	48
$n\text{-C}_3\text{H}_7$	$(\text{C}_6\text{H}_5)_3\text{P}$?	4A	48
$n\text{-C}_3\text{H}_7$	$(n\text{-C}_4\text{H}_9)_3\text{P}$?	1A	48
HOCH_2CH_2	H_2O	ClO_4^-	1A, d	155
CH_3CO	MeIMD	ClO_4^-	1A, a, d	16
$\text{C}_6\text{H}_5\text{CH}_2$	H_2O	I^-		42
$\text{C}_6\text{H}_5\text{CH}_2$	H_2O	ClO_4^-		42
$\text{C}_6\text{H}_5\text{CH}_2$	IMD	ClO_4^-	2A, d	46
$\text{C}_6\text{H}_5\text{CH}_2$	MeIMD	ClO_4^-	1A, d	46

TABLE III *continued*
 8. $L_4 = (DO)(DOH)pn$

R	X	Anion	Prep. and characterization	References
$C_6H_5CH_2$	$C_7H_6N_2$?	4A	48
$C_6H_5CH_2$	$(C_6H_5)_3P$?	4A	48
$C_6H_5CH_2$	I^-	—		42
$C_6H_5CH_2$	$C_6H_5CH_2^-$	—	1A, 3A, 4A, d	42
C_6H_5	H_2O	ClO_4^-	d	46
C_6H_5	IMD	?	4A	48
C_6H_5	$C_7H_6N_2$?	4A	48
C_6H_5	DMF	?		50
C_6H_5	$(C_6H_5)_3P$?	4A	48
C_6H_5	I^-	—	d	46
C_6H_5	Br^-	—	3A, d	46
C_6H_5	CH_3^-	—	1A, 4A	42

9. $L_4 = (G)_2$

R	X	Prep. and characterization	References
CH_3	py	1A, c, d	154, 161
CH_3	$(n-C_4H_9)_3P$	1A	147

10. $L_4 = (DMG)_2$

R	X	Prep. and characterization	References
CH_3	—	4A, b, d	80, 161
CH_3	H_2O	1A, 4A, b, c, d	146, 161
CH_3	OH^-	4A	52
CH_3	NH_3	1A, c, d	154
CH_3	py	1A, 4A, b, c, d	146, 161, 163, 164
CH_3	IMD	1A, c, d	154
CH_3	$C_7H_6N_2$	1A, c, d	161
CH_3	2-pic	1A, c, d	154
CH_3	$(CH_3)_3N$	4A	116a
CH_3	$C_6H_5NH_2$	d	161
CH_3	2,4- $(CH_3)_2C_6H_3NH_2$	b	70a
CH_3	N_3^-	4A	52
CH_3	NCS^-	4A	1, 52, 143
CH_3	CH_3CN	4A, b	116a
CH_3	$(CH_3O)_3P$	4A, b, d	116a, 161

TABLE III *continued*10. $L_4 = (\text{DMG})_2$

R	X	Prep. and characterization	References
CH ₃	(C ₆ H ₅ O) ₃ P		158
CH ₃	(<i>n</i> -C ₄ H ₉) ₃ P	1A, b, d	161, 164
CH ₃	(C ₆ H ₅) ₃ P	1A, 3A, a, b, c, d	142, 151, 161
CH ₃	CN ⁻		158
CH ₃	cyclo-C ₆ H ₁₁ NC	c	158
CH ₃	CH ₃ NC	4A, a, b, d	80
CH ₃	CO	4A, a, b	80
CH ₃	Cl ⁻	4A	52
CH ₃	I ⁻	4A	52
CH ₃	SO ₂	4A, a, b, c, d	98
CH ₃	DMSO	4A	116a
CH ₃	DPSO	4A	116a
CH ₃	S(CH ₂ CH ₂) ₂ O	4A	116a
CH ₃	(CH ₃) ₂ S	1A, d	146, 161
CH ₃	(C ₂ H ₅) ₂ S	1A, d	161
CH ₃	(C ₆ H ₅) ₃ As	c	158
CH ₃	(C ₆ H ₅) ₃ Sb	c	158
CD ₃	py	4A, d	161
CD ₃	(C ₆ H ₅) ₃ P	1A, a, b, d	142
C ₂ H ₅	—	d	161
C ₂ H ₅	H ₂ O	c, d	161
C ₂ H ₅	NH ₃	c, d	154
C ₂ H ₅	py	1A, a, b, c, d	161
C ₂ H ₅	IMD	c, d	154
C ₂ H ₅	C ₇ H ₆ N ₂	c, d	154
C ₂ H ₅	2-pic	1A	147
C ₂ H ₅	2,6-lut	1A	147
C ₂ H ₅	4CN-py	1A	147
C ₂ H ₅	C ₆ H ₅ NH ₂	1A	147
C ₂ H ₅	N ₃ ⁻	4A	52
C ₂ H ₅	NCS ⁻	4A	52
C ₂ H ₅	cyclo-C ₆ H ₁₁ NH ₂	1A	147
C ₂ H ₅	(C ₆ H ₅) ₃ P	1A, 3A, a, b, c, d	151
C ₂ H ₅	(<i>n</i> -C ₄ H ₉) ₃ P	c	158
C ₂ H ₅	CN ⁻	1A	147
C ₂ H ₅	cyclo-C ₆ H ₁₁ NC	1A	147
C ₂ H ₅	(CH ₃) ₂ S	1A	147
C ₂ H ₅	(C ₆ H ₅) ₃ As	1A, c	147
C ₂ H ₅	(C ₆ H ₅) ₃ Sb	1A, c	147
<i>n</i> -C ₃ H ₇	H ₂ O	1A, c, d	161
<i>n</i> -C ₃ H ₇	py	1A, a, b, c, d	161
<i>n</i> -C ₃ H ₇	C ₇ H ₆ N ₂	c	154

TABLE III *continued*10. $L_4 = (\text{DMG})_2$

R	X	Prep. and characterization	References
<i>n</i> -C ₃ H ₇	(<i>n</i> -C ₄ H ₉) ₃ P	1A	147
<i>n</i> -C ₃ H ₇	(C ₆ H ₅) ₃ P	1A, a, b, c, d	154
<i>n</i> -C ₃ H ₇	cyclo-C ₆ H ₁₁ NC	c, d	154
<i>n</i> -C ₃ H ₇	(C ₆ H ₅) ₃ As	c, d	154
<i>n</i> -C ₃ H ₇	(C ₆ H ₅) ₃ Sb	c, d	154
<i>i</i> -C ₃ H ₇	H ₂ O	c	158
<i>i</i> -C ₃ H ₇	py	1A, 1B, b, d	68, 161
<i>i</i> -C ₃ H ₇	IMD	c, d	154
<i>i</i> -C ₃ H ₇	N ₃ ⁻	4A	52
<i>i</i> -C ₃ H ₇	NCS ⁻	4A	52
<i>i</i> -C ₃ H ₇	(<i>n</i> -C ₄ H ₉) ₃ P	1A	147
<i>n</i> -C ₄ H ₉	H ₂ O		1
<i>n</i> -C ₄ H ₉	py	1A, 4A, a, b, c, d	151
<i>n</i> -C ₄ H ₉	(<i>n</i> -C ₄ H ₉) ₃ P	1A	147
CH ₃ CH(CH ₃)CH ₂	H ₂ O	c, d	154
CH ₃ CH(CH ₃)CH ₂	py	b, d	68, 161
CH ₃ CH(CH ₃)CH ₂	IMD	d	154
CH ₃ CH(CH ₃)CH ₂	C ₇ H ₆ N ₂	d	154
CH ₃ CH ₂ CH(CH ₃)	(<i>n</i> -C ₄ H ₉) ₃ P	1A	147
<i>n</i> -C ₅ H ₁₁	py	b	68
<i>n</i> -C ₅ H ₁₁	(<i>n</i> -C ₄ H ₉) ₃ P	1A	147
(CH ₃) ₂ CHCH ₂ CH ₂	py		160
(CH ₃) ₂ CHCH ₂ CH ₂	(<i>n</i> -C ₄ H ₉) ₃ P	1A	147
(CH ₃) ₂ CHCH(CH ₃)	(<i>n</i> -C ₄ H ₉) ₃ P	1A	147
(CH ₃) ₃ CHCH ₂	py	d	161
(CH ₃) ₃ CHCH ₂	(<i>n</i> -C ₄ H ₉) ₃ P	1A	147
<i>n</i> -C ₆ H ₁₃	py	d	161
<i>n</i> -C ₆ H ₁₃	(<i>n</i> -C ₄ H ₉) ₃ P	1A	147
(CH ₃) ₂ CH(CH ₂) ₄ CH ₂	py	1A	55
C ₆ H ₅ CH ₂	py	1A, 3A, a, b, d	142, 151
C ₆ H ₅ CH ₂	γ-pic	2A	144
C ₆ H ₅ CH ₂	nic	2A	144
C ₆ H ₅ CH ₂	(C ₆ H ₅) ₃ P	1A, 3A, d	151, 163
C ₆ H ₅ CH ₂	(<i>n</i> -C ₄ H ₉) ₃ P	1A	147
<i>p</i> - <i>t</i> -C ₄ H ₉ C ₆ H ₄ CH ₂	(<i>n</i> -C ₄ H ₉) ₃ P	1A	147
C ₆ H ₅ CH(C ₂ H ₅)	py	b, d	58
<i>p</i> -CH ₃ C ₆ H ₄ CH(CH ₃)	py	b, d	58
C ₆ H ₅ CH ₂ CH ₂	py	1A, d	151
C ₆ H ₅ CH(CH ₃)	H ₂ O	1B, d	163
C ₆ H ₅ CH(CH ₃)	py	1B, b, d	163
C ₆ H ₅ CH(CH ₃)	(<i>n</i> -C ₄ H ₉) ₃ P	1A	147
(C ₆ H ₅) ₂ CH	(<i>n</i> -C ₄ H ₉) ₃ P	1A	147

TABLE III *continued*10. $L_4 = (\text{DMG})_2$

R	X	Prep. and characterization	References
$\text{CH}_2=\text{CHCH}_2$	py	b	58, 175
$\text{CH}_3\text{CH}=\text{CHCH}_2$	py	1B, a, b, d	58, 161
$\text{CH}_2=\text{CHCH}(\text{CH}_3)$	$(n\text{-C}_4\text{H}_9)_3\text{P}$	1A	147
$\text{CH}_2=\text{CH}=\text{CH}$	py	1A, a, b	99
$\text{CH}_2=\text{CH}$	py	1A, 1B, d	151, 163
$\text{CH}_2=\text{CH}$	$\text{C}_6\text{H}_5\text{NH}_2$	1B, d	129
$\text{CH}_2=\text{CH}$	$(\text{CH}_3\text{O})_3\text{P}$	4A, d	129
$\text{C}_6\text{H}_5\text{CH}=\text{CH}$	H_2O	1A, b, d	59, 163
$\text{C}_6\text{H}_5\text{CH}=\text{CH}$	py	1A, b, d	59, 129, 151
$\text{C}_6\text{H}_5\text{CH}=\text{CH}$	$\text{C}_6\text{H}_5\text{NH}_2$	1A, b, d	59
$\text{C}_6\text{H}_5\text{CH}=\text{CH}$	$(\text{CH}_3\text{O})_3\text{P}$	4A, b, d	129
$\text{CH}_2=\text{CH}(\text{C}_6\text{H}_5)$	py	1B, b, d	59, 129
$\text{CH}_2=\text{CH}(\text{C}_6\text{H}_5)$	$(\text{C}_2\text{H}_5\text{O})_3\text{P}$	4A, b, d	129
$\text{CHD}=\text{CH}(\text{C}_6\text{H}_5)$	py	1B, b, d	129
$\text{C}_6\text{H}_5\text{C}\equiv\text{C}$	py	3A, c, d	151
$\text{Co}-\text{CH}_2\text{CH}_2\text{CH}_2-\text{Co}$	py	1A, d	161
$\text{Co}-\text{CH}_2(\text{CH}_2)_2\text{CH}_2-\text{Co}$	py	1A, d	161, 162
$\text{Co}-\text{CH}=\text{CH}-\text{Co}$	H_2O	1B, d	163
$\text{Co}-\text{CH}=\text{CH}-\text{Co}$	py	1B, d	163
C_6H_5	py	3A, c, d	146, 151
C_6H_5	$(\text{CH}_3)_3\text{N}$	3A, d	151
C_6H_5	$(\text{C}_6\text{H}_5)_3\text{P}$	3A, d	151
C_6H_5	$(n\text{-C}_4\text{H}_9)_3\text{P}$	3A, d	151
$p\text{-CH}_3\text{C}_6\text{H}_4$	py	c, d	154, 181
cyclo- C_3H_5	$(n\text{-C}_4\text{H}_9)_3\text{P}$	1A	147
cyclo- C_4H_7	$(n\text{-C}_4\text{H}_9)_3\text{P}$	1A	147
cyclo- C_5H_9	$(n\text{-C}_4\text{H}_9)_3\text{P}$	1A	147
cyclo- C_6H_{11}	py	c, d	154
cyclo- C_6H_{11}	$(n\text{-C}_4\text{H}_9)_3\text{P}$	1A	147
cyclo- C_7H_{13}	$(n\text{-C}_4\text{H}_9)_3\text{P}$	1A	147
cyclo- C_8H_{15}	$(n\text{-C}_4\text{H}_9)_3\text{P}$	1A	147
cyclo- $\text{C}_6\text{H}_7\text{D}_4$	py	b, d	95
NCCH_2	py	1A, d	163
NCCH_2	$(n\text{-C}_4\text{H}_9)_3\text{P}$	1A	147
NCCH_2CH_2	py	1A, 1B, c, d	151, 163
$\text{NCCH}(\text{CH}_3)$	py	1B, 4B, b, c, d	163
$\text{NCCH}(\text{CH}_3)$	$\text{C}_6\text{H}_5\text{NH}_2$	1B, 4B, d	163
$\text{NCCH}(\text{CH}_3)$	$(n\text{-C}_4\text{H}_9)_3\text{P}$	1B, d	163
$\text{NCCH}(\text{CH}_3)\text{CH}_2$	py	1B, d	163
$\text{NCCH}(\text{CH}_3)\text{CH}_2$	$\text{C}_6\text{H}_5\text{NH}_2$	1B, 4B, d	163
$\text{NCCH}(\text{C}_2\text{H}_5)$	py	1B, d	163
$\text{NCCH}_2\text{CH}(\text{CN})$	py	1B, b, d	163

TABLE III *continued*10. $L_4 = (DMG)_2$

R	X	Prep. and characterization	References
NCCH ₂ CH(CN)	(<i>n</i> -C ₄ H ₉) ₃ P		159
NCC(CH ₃) ₂	py	1B	163
NCCH ₂ CH(CH ₃)	py		159
NCCD ₂ CD ₂	py	1B	159
ClCH ₂	—	4A, d	163
ClCH ₂	H ₂ O	1A, d	163
ClCH ₂	py	1A, d	163
ClCH ₂	(CH ₃) ₂ S	1A, d	163
ICH ₂	py	1A, d	163
Br(CH ₂) ₂ CH ₂	py	1A, d	161
Cl(CH ₂) ₂ CH ₂	(<i>n</i> -C ₄ H ₉) ₃ P	1A	147
Br(CH ₂) ₃ CH ₂	py	1A, d	162
Br(CH ₂) ₃ CH ₂	(<i>n</i> -C ₄ H ₉) ₃ P	1A	147
1-Cl-nap	(<i>n</i> -C ₄ H ₉) ₃ P	1A	147
cyclo-4-Br-C ₆ H ₁₀	py	1A, b, d	95
<i>p</i> -FC ₆ H ₄ CH(CH ₃)	py	1B, b	58
<i>p</i> -ClC ₆ H ₄ CH(CH ₃)	py	1B, b	58
<i>p</i> -BrC ₆ H ₄ CH(CH ₃)	py	1B, b	58
ClCH ₂ CH(CH ₂ OH)	py	1A, a, b, d	142
ClCH ₂ Hg	H ₂ O	4B	1
<i>p</i> -ClC ₆ H ₄	py		181
CF ₃	py	1A, c, d	154, 161
CF ₃ CH ₂	py	1A, a, b, d	81a
CF ₃ CH ₂	(C ₆ H ₅) ₃ P	1A, a, b, d	81a
CF ₃ CH=CH	py	1B, b, d	129
CF ₃ CH=CH	(CH ₃ O) ₃ P	4A, b, d	129
HOCH ₂ CH ₂	H ₂ O	1A, d	162
HOCH ₂ CH ₂	py	1A, b, d	129, 162
HOCH ₂ CH ₂	C ₇ H ₆ N ₂	4A, d	162
HOCH ₂ CH ₂	(C ₆ H ₅) ₃ P	4A, d	162
HOCH ₂ CH ₂	(<i>n</i> -C ₄ H ₉) ₃ P	1A	147, 162
HOCH ₂ CH ₂ CH ₂	py	1A, 1B, d	162
HOCH(CH ₃)CH ₂	py	1A, d	69, 162
HOCH ₂ (CH ₂) ₂ CH ₂	py	1A, d	162
cyclo-2—HO—C ₆ H ₁₀	py	1A, b, d	95, 162
HOCH(<i>n</i> -C ₆ H ₁₃)CH ₂	py	1A, d	162
HOCH ₂ CH(OH)CH ₂	py	1A, d	162
HOCH(C ₆ H ₅)CH ₂	py	1A, d	162
HOCH ₂ CH(CH ₃)	?		162
HOCH ₂ CH(C ₆ H ₅)	py	1A, b, d	129
HOC(CH ₃) ₂ CH ₂	py	1A, d	155
HOCD ₂ CH(C ₆ H ₅)	py	1A, b, d	129

TABLE III *continued*10. $L_4 = (\text{DMG})_2$

R	X	Prep. and characterization	References
$\text{HOCH}(\text{CH}_3)\text{CD}_2$	py		155
CH_3OCH_2	$(n\text{-C}_4\text{H}_9)_3\text{P}$	1A	147
$\text{CH}_3\text{OCH}_2\text{CH}_2$?		163
$\text{CH}_3\text{OCH}_2\text{CH}_2$	py		69
$\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2$	py	1A, 3A, b, d	162
$(\text{CH}_3\text{O})_2\text{CHCH}_2$	py	1A, d	163
$\text{HOCH}_2\text{CH}=\text{CH}$	py	1B, b, d	59
$\text{HOCH}_2\text{C}=\text{CH}_2$	py	1B, b, d	59
$p\text{-CH}_3\text{OC}_6\text{H}_4$	py	3A, c, d	151, 154
$2\text{-CH}_3\text{OC}_6\text{H}_{10}$	py	1A, b, d	95
CH_3CO	MeIMD	1A, a, d	16
$\text{C}_6\text{H}_5\text{CO}$	$(n\text{-C}_4\text{H}_9)_3\text{P}$	1A, d	163
$\text{CH}_3\text{COCH}(\text{CH}_3)$	py	1B, a, b, d	163
CH_3COCH_2	py	1B, a, b, d	163
$\text{C}_6\text{H}_5\text{COCH}_2$	py	1A, d	163
$\text{OHC}-\text{CH}_2$	py	4B, c, d	163
NH_2COCH_2	$(n\text{-C}_4\text{H}_9)_3\text{P}$	1A	147
$\text{CH}_2\text{COOC}_2\text{H}_5$			
	H_2O	1B, d	163
$\text{CH}(\text{COOC}_2\text{H}_5)$			
$\text{CH}_2\text{COOC}_2\text{H}_5$			
	py	1B, d	163
$\text{CH}(\text{COOC}_2\text{H}_5)$			
$\text{CH}_3\text{OOCCH}(\text{CH}_3)$	H_2O	1B, d	163
$\text{CH}_3\text{OOCCH}(\text{CH}_3)$	py	1B, d	163
$\text{CH}_3\text{OOCCH}(\text{CH}_3)$	$(n\text{-C}_4\text{H}_9)_3\text{P}$	1B, d	163
$\text{CH}_3\text{COOCH}(\text{CH}_3)$	py	1B, d	163
$\text{CH}_3\text{OOCCH}_2\text{CH}_2$	py	1B, d	163
$\text{CH}_3\text{OOCCH}_2\text{CH}_2$	$(n\text{-C}_4\text{H}_9)_3\text{P}$	4A, d	163
$\text{C}_2\text{H}_5\text{OOCCH}_2\text{CH}_2$	py	1B, d	163
$\text{C}_2\text{H}_5\text{OOCCH}(\text{CH}_3)$	H_2O	b	163
$\text{C}_2\text{H}_5\text{OOCCH}(\text{CH}_3)$	py	1B, d	163
$\text{C}_2\text{H}_5\text{OOCCH}(\text{CH}_3)$	NH_3	4A, d	163
$\text{CH}_3\text{OOCCH}(\text{CH}_3)\text{CH}_2$	py	1B, d	163
$\text{C}_2\text{H}_5\text{OOCCH}(\text{CH}_3)\text{CH}_2$	py	1A, d	163
$\text{CH}_3\text{OOCCH}_2$	py	1A, a, b, c, d	142, 163
$\text{CH}_3\text{OOCCH}_2$	$\text{C}_7\text{H}_6\text{N}_2$	4A, d	163
$\text{CH}_3\text{OOCCH}_2\text{CH}(\text{CH}_3)$	—	d	163
$\text{CH}_3\text{OOCCH}_2\text{CH}(\text{CH}_3)$	py	1A, d	163
CH_3OCO	py	4D, d	44
$\text{C}_2\text{H}_5\text{OOCCH}=\text{CH}$	H_2O	1B, d	163
$\text{C}_2\text{H}_5\text{OOCH}=\text{CH}$	py	1A, a, b, d	59, 163

TABLE III *continued*10. $L_4 = (\text{DMG})_2$

R	X	Prep. and characterization	References
$\text{C}_2\text{H}_5\text{OOCCH}=\text{CH}$ CHCOOCH_3	$(\text{C}_2\text{H}_5\text{O})_3\text{P}$	4A, b, d	129
\parallel $\text{C}(\text{COOCH}_3)$ CHCOOCH_3	py	1B, a, b, d	129, 163
\parallel $\text{C}(\text{COOCH}_3)$ $\text{C}_2\text{H}_5\text{OOCCH}=\text{C}(\text{CH}_3)$	$(\text{CH}_3\text{O})_3\text{P}$	4A, b, d	129
$\text{C}_2\text{H}_5\text{OOCCH}=\text{C}(\text{CH}_3)$	py	1B, a, b, d	129
$\text{C}_2\text{H}_5\text{OOCCH}=\text{C}(\text{CH}_3)$	$\text{C}_6\text{H}_5\text{NH}_2$	1B, a, b, d	129
$\text{C}_2\text{H}_5\text{OOCCH}=\text{C}(\text{CH}_3)$	$(\text{CH}_3\text{O})_3\text{P}$	4A, b, d	129
$\text{CH}_3\text{OOCCH}=\text{CH}$	py	1A, 1B, a, b, d	59
HOOCCH_2	—	—	164
HOOCCH_2	py	4B, d	163
$\text{HOOCCH}(\text{CH}_3)$	—	—	163
$\text{HOOCCH}(\text{CH}_3)$	H_2O	1B, d	163
$\text{HOOCCH}(\text{CH}_3)$	py	1B, 4A, a, b, d	163
$\text{HOOCCH}_2\text{CH}_2$	—	—	163
$\text{HOOCCH}_2\text{CH}_2$	py	4B, a, d	163
CH_2COOH	—	—	163
\mid $\text{CHCOOC}_2\text{H}_5$ CH_2COOH	—	4B	163
\mid $\text{CHCOOC}_2\text{H}_5$ OOCCH_2	py	4B, d	163
OOCCH_2	$(n\text{-C}_4\text{H}_9)_3\text{P}$	1A	147
Adenosyl	H_2O	1A	155
Adenosyl	py	1A, c, d	155, 183
2',3'-Di-O-acetyl-5'- deoxyadenosyl	py	1A, a	142
2',3'-Isopropylidene-5'- deoxyadenosyl	py	1A	155
Dihydrouridyl and derivatives	py	1B	18
Dihydrouridyl and derivatives	$(\text{C}_6\text{H}_5)_3\text{P}$	1B	18

TABLE III *continued*11. $L_4 = (\text{DPG})_2$

R	X	Prep. and characterization	References
CH ₃	H ₂ O	1A, c	154
CH ₃	NH ₃	1A, c	154
CH ₃	py	1A, c	154, 158
CH ₃	IMD	1A, c	154
CH ₃	C ₇ H ₆ N ₂	1A, c	154
CH ₃	(<i>n</i> -C ₄ H ₉) ₃ P	1A, c	154
CH ₃	(C ₆ H ₅) ₃ P	1A, c	154
CH ₃	cyclo-C ₆ H ₁₁ NC	1A, c	154
CH ₃	CN ⁻	1A, c	154
C ₂ H ₅	H ₂ O	1A, c	154
C ₂ H ₅	NH ₃	1A, c	154
C ₂ H ₅	py	1A, c	154
C ₂ H ₅	piperidine	1A, c	154
C ₂ H ₅	(C ₂ H ₅) ₃ N	1A, c	154
C ₂ H ₅	C ₆ H ₅ NH ₂	1A, c	154
C ₂ H ₅	IMD	1A, c	154
C ₂ H ₅	C ₇ H ₆ N ₂	1A, c	154
C ₂ H ₅	CH ₃ CN	1A, c	154
<i>n</i> -C ₃ H ₇	py	1A	147
<i>n</i> -C ₃ H ₇	(<i>n</i> -C ₄ H ₉) ₃ P	1A	147
<i>n</i> -C ₃ H ₇	(CH ₃) ₂ S	1A	147
Dihydrouridyl and derivatives }	py	1B	18
	(C ₆ H ₅) ₃ P	1B, a, b, c, d	18
C ₆ H ₅ CH ₂	py	2A	144

12. $L_4 = (\text{DMPG})_2$

R	X	Prep. and characterization	Reference
C ₆ H ₅ CH ₂	py	2A	144

13. $L_4 = (\text{DNPG})_2$

R	X	Prep. and characterization	Reference
C ₆ H ₅ CH ₂	py	2A	144

TABLE III *continued*14. $L_4 = (\text{CPD})_2$

R	X	Prep. and characterization	References
$n\text{-C}_3\text{H}_7$	—	1A	147
$n\text{-C}_3\text{H}_7$	py	1A	147
$n\text{-C}_3\text{H}_7$	$(n\text{-C}_4\text{H}_9)_3\text{P}$	1A	147
$n\text{-C}_3\text{H}_7$	$(\text{CH}_3)_2\text{S}$	1A	147

15. $L_4 = (\text{CHD})_2$

R	X	Prep. and characterization	References
CH_3	py	1A, 4C, c, d	154, 161
$n\text{-C}_3\text{H}_7$	—	1A	147
$n\text{-C}_3\text{H}_7$	py	1A	147
$n\text{-C}_3\text{H}_7$	$(n\text{-C}_4\text{H}_9)_3\text{P}$	1A	147
$n\text{-C}_3\text{H}_7$	$(\text{CH}_3)_2\text{S}$	1A	147

16. $L_4 = (\text{DMG} - \text{BF}_2)_2$

R	X	Prep. and characterization	References
CH_3	—	4C	147
CH_3	H_2O	4C, d	161
CH_3	py	4C, d	161
C_2H_5	—		147
C_2H_5	H_2O		158
C_2H_5	py		158
$n\text{-C}_3\text{H}_7$	H_2O		158
HOCH_2CH_2	—	1A	155
HOCH_2CH_2	py	1A	155

17. $L_4 = \text{BAE}$

R	X	Prep. and characterization	References
CH_3	—	3A, b, c, d	49
CH_3	H_2O	1A, 2A, 3A, d	40, 49
CH_3	en	4A	49
CH_3	py	4A, b, d	40, 49

TABLE III *continued*17. $L_4 = \text{BAE}$

R	X	Prep. and characterization	References
CH_3	4CN-py	b	83
CH_3	4Me-py	b	83
CH_3	piperidine	b	83
CH_3	$\text{C}_7\text{H}_6\text{N}_2$	4A, d	40
CH_3	$\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$	4A	49
$[\text{CH}_3\text{Co}^{\text{III}}(\text{BAE})\text{NH}_2\text{CH}_2-]_2$	—	4A, d	40
CH_3	$(\text{C}_6\text{H}_5)_3\text{P}$	b	83
C_2H_5	—	3A, b, c, d	49
C_2H_5	H_2O	1A, 3A, d	40, 49
C_2H_5	py	4A, b, c	40, 49, 83, 131
C_2H_5	en	4A	49
C_2H_5	$\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$	4A	49
$n\text{-C}_3\text{H}_7$	—	4A, c, d	40
$n\text{-C}_3\text{H}_7$	H_2O	1A, d	40
$n\text{-C}_3\text{H}_7$	py	4A, c	40
$\text{CH}_2=\text{CH}$	—	1A, 1B, 4A, b, c, d	40
$\text{CH}_2=\text{CH}$	py	4A, b, c, d	40, 83
$\text{CH}_2=\text{CH}$	DMF		50
$\text{Co}-\text{CH}_2\text{CH}_2-\text{Co}$	py	c	40
$\text{Co}-\text{CH}_2(\text{CH}_2)_2\text{CH}_2-\text{Co}$	—	1A, c, d	40
$\text{Br}(\text{CH}_2)_3\text{CH}_2$	—	4A, c, d	40
$\text{Br}(\text{CH}_2)_3\text{CH}_2$	H_2O	1A, d	40
NCCH_2CH_2	—	1B, c, d	40
NCCH_2CH_2	py	4A, c, d	40
CH_3CO	—	1A, a, c, d	40
CH_3CO	py	4A, a, c, d	40
CH_3OCO	H_2O	4D, d	44
C_2F_5	H_2O	1A	174a
C_6H_5	—	3A, b, c, d	49, 82, 83
C_6H_5	H_2O	3A, d	49
C_6H_5	py	3A, b, d	49
C_6H_5	D^5py		82
C_6H_5	piperidine		82
C_6H_5	$\text{C}_7\text{H}_6\text{N}_2$	4A, d	40
C_6H_5	en	4A	49
$[\text{C}_6\text{H}_5\text{Co}^{\text{III}}(\text{BAE})\text{NH}_2\text{CH}_2-]_2$	—	4A, d	40
$[\text{C}_6\text{H}_5\text{Co}^{\text{III}}(\text{BAE})]_2\text{C}_4\text{H}_{10}\text{N}_2$	—	4A, d	40
C_6H_5	$\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$	4A, d	49
$p\text{-CH}_3\text{C}_6\text{H}_4$	—	b	82
$p\text{-CH}_3\text{C}_6\text{H}_4$	D^5py	b	82
$p\text{-BrC}_6\text{H}_4$	—	b	82

TABLE III *continued*17. $L_4 = \text{BAE}$

R	X	Prep. and characterization	References
<i>p</i> -BrC ₆ H ₄	D ⁵ py	b	82
<i>p</i> -BrC ₆ H ₄	piperidine	b	82
<i>p</i> -IC ₆ H ₄	—	b	82
<i>p</i> -IC ₆ H ₄	D ⁵ py	b	82
<i>p</i> -IC ₆ H ₄	piperidine	b	82
<i>p</i> -NCC ₆ H ₄	—	b	82
<i>p</i> -NCC ₆ H ₄	D ⁵ py	b	82
<i>p</i> -NCC ₆ H ₄	piperidine	b	82
<i>p</i> -NO ₂ C ₆ H ₄	—	b	82
<i>p</i> -NO ₂ C ₆ H ₄	D ⁵ py	b	82
<i>p</i> -NO ₂ C ₆ H ₄	piperidine	b	82
<i>p</i> -CH ₃ OC ₆ H ₄	—	b	82
<i>p</i> -CH ₃ OC ₆ H ₄	D ⁵ py	b	82

18. $L_4 = \text{tfen}$

R	X	Prep. and characterization	References
CH ₃	—	4C, b	174a
CH ₃	H ₂ O	1A	174a
C ₂ H ₅	—	4C, b	174a
C ₂ H ₅	H ₂ O	1A	174a

19. $L_4 = \text{salen}$

R	X	Prep. and characterization	References
CH ₃	—	4A, b, c, d	26, 43, 47, 64
CH ₃	H ₂ O	1A, 3A, a, b, c, d	26, 37, 43, 47, 64
CH ₃	NH ₃	4A, c, d	47
CH ₃	py	1A, 3A, a, b, c, d	47, 64
CH ₃	C ₇ H ₆ N ₂	3A, c, d	47
CH ₃	DMF		50
C ₂ H ₅	—	1A, 3A, b, c, d	43, 47
C ₂ H ₅	NH ₃	4A	158
C ₂ H ₅	py	3A, c, d	47, 64
C ₂ H ₅	DMF		50

TABLE III *continued*19. L_4 = salen

R	X	Prep. and characterization	References
$n\text{-C}_3\text{H}_7$	—		147
$n\text{-C}_3\text{H}_7$	H_2O	1A, 3A, c, d	43, 47
$n\text{-C}_3\text{H}_7$	NH_3	4A	47
$n\text{-C}_3\text{H}_7$	py	3A, c	47
$i\text{-C}_3\text{H}_7$	H_2O	1A, d	158
$i\text{-C}_3\text{H}_7$	py	1A, b, d	64
$n\text{-C}_4\text{H}_9$	H_2O	3A, c, d	47
$n\text{-C}_4\text{H}_9$	NH_3	4A	47
$n\text{-C}_4\text{H}_9$	py	1A, 3A, b, c, d	47, 64
$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2$	H_2O	1A, d	158
$\text{C}_6\text{H}_5\text{CH}_2$	py	1A, b, d	64
$\text{CH}_2=\text{CH}$	H_2O	1A, 1B, c, d	43
$\text{CH}_2=\text{CH}$	py	4A, c, d	43
$\text{CH}_2=\text{CH}$	DMF		50
C_6H_5	—	4A, c, d	47
C_6H_5	H_2O	3A, b, c, d	47
C_6H_5	NH_3	4A, d	47
C_6H_5	py	3A, c, d	47, 64
C_6H_5	DMF		50
$p\text{-CH}_3\text{C}_6\text{H}_4$	H_2O		128
NCCCH_2	CH_3OH		30
NCCH_2CH_2	H_2O	1A, 1B, c, d	43
NCCH_2CH_2	py	4A, c, d	43
$(\text{NC})_2\text{CH}$	polymeric	3B	4
$(\text{NC})_2\text{CH}$	H_2O	3B	4
$(\text{NC})_2\text{CH}$	py	3B	4
ClCH_2	H_2O	1A, d	158
$\text{BrCH}_2(\text{CH}_2)_2\text{CH}_2$	H_2O	1A, c, d	43
$n\text{-C}_3\text{F}_7$	—	4B	174a
C_6F_5	py	1A, d	53
C_6F_5	SO_2 , dimeric	4A	53
HOCH_2CH_2	—	1A, d	155
HOCH_2CH_2	H_2O	1A, d	155
O_2NCH_2	H_2O	3B, c, d	16
CH_3COCH_2	CH_3OH	3B, a, c, d	16
$p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2$	MeIMD	2B	118
CH_3CO	—	1A, a, b, c, d	17, 43
CH_3CO	H_2O	1A, a, c, d	37
CH_3CO	py	1A, a, b, c, d	43, 64
$\text{C}_2\text{H}_5\text{CO}$	—	1A, a, b, c, d	17
$i\text{-C}_3\text{H}_7\text{CO}$	H_2O	1A, a, b, c, d	17
$\text{C}_6\text{H}_5\text{CH}_2\text{CO}$	H_2O	1A, a, b, c, d	17

TABLE III *continued*19. $L_4 = \text{salen}$

R	X	Prep. and characterization	References
CH_3OCO	H_2O	1A, 4D, a, c, d	37, 38, 43, 44
CH_3OCO	py	4A, c, d	43
$\text{C}_2\text{H}_5\text{OCO}$	H_2O	1A, 4D, c, d	38, 43, 44
$\text{C}_2\text{H}_5\text{OCO}$	py	4A, c, d	43
<i>i</i> - $\text{C}_3\text{H}_7\text{OCO}$	H_2O	4D, c, d	38, 44
$\text{C}_6\text{H}_5\text{O}_3$	—	3B, c, d	16
acac	—	3B, c, d	16

20. $L_4 = 7\text{-Me-salen}$

R	X	Prep. and characterization	References
CH_3	—	1A, d	16
C_2H_5	—	1A, d	16
CH_3COCH_2	—	3B, d	16
O_2NCH_2	CH_3OH	3B, d	16
$\text{C}_6\text{H}_5\text{O}_3$	—	3B, d	16
acac	—	3B, d	16
$\text{CH}_2=\text{CH}$	—	1B, d	16
$\text{CH}_2=\text{CH}$	DMF	—	50
CH_3CO	—	1A, a, d	16
CH_3OCO	H_2O	1A, d	16
C_6H_5	—	1A, d	16
<i>p</i> - $\text{O}_2\text{NC}_6\text{H}_4\text{CH}_2$	MeIMD	2B	118

21. $L_4 = 7\text{-Ph-salen}$

R	X	Prep. and characterization	Reference
CH_3OCO	H_2O	4D	44

TABLE III *continued*22. L_4 = saloph

R	X	Prep. and characterization	References
CH ₃	—	1A, a, b, d	16
CH ₃	H ₂ O	1A, b, d	16
CH ₃	THF	1A, b	16
CH ₃ CO	—	1A, a, b, d	16
CH ₃ CO	H ₂ O	1A, a, b, d	16, 17
CH ₃ OCO	H ₂ O	1A, 4D, d	16, 44
O ₂ NCH ₂	H ₂ O	3B, d	16
C ₆ H ₅	H ₂ O		16
<i>p</i> -NCC ₆ H ₄ CH ₂	H ₂ O	2A, d	119
<i>p</i> -NCC ₆ H ₄ CH ₂	MeIMD	2A	119
<i>p</i> -NCC ₆ H ₄ CH ₂	(<i>n</i> -C ₄ H ₉) ₃ P	2A	119
<i>p</i> -NCC ₆ H ₄ CH ₂	(C ₆ H ₅) ₃ P	2A	119
<i>p</i> -O ₂ NC ₆ H ₄ CH ₂	IMD	2B	118
<i>p</i> -O ₂ NC ₆ H ₄ CH ₂	MeIMD	2B	118
<i>p</i> -O ₂ NC ₆ H ₄ CH ₂	C ₆ H ₅ CH ₂ NH ₂	2B	118
<i>o</i> -O ₂ NC ₆ H ₄ CH ₂	IMD	2B	118

23. L_4 = 4-Cl-saloph

R	X	Reference
<i>p</i> -O ₂ NC ₆ H ₄ CH ₂	IMD	118

24. L_4 = napsälen

R	X	Prep. and characterization	Reference
CH ₃ CO	H ₂ O	1A, a, c, d	17

25. L_4 = napsaloph

R	X	Prep. and characterization	Reference
CH ₃ CO	anhydrous	1A, a, c, d	17

TABLE III *continued*26. $L_4 = \text{salpn-1,3}$

R	X	Prep. and characterization	References
CH_3	H_2O	1A, d	158
C_2H_5	H_2O	1A, d	158
CH_3OCO	H_2O	4D, d	44

27. $L_4 = \text{salpn-1,2}$

R	X	Prep. and characterization	Reference
$\text{CH}(\text{CN})_2$	py	3B, d	4

28. Pentacyanide Complexes

R	Prep. and characterization	References
CH_3	1A, a, b, d	74, 109
C_2H_5	1A, a, b	74, 109
$n\text{-C}_3\text{H}_7$	1A, a, d	74, 109, 110
$i\text{-C}_3\text{H}_7$	1A, a	108
$n\text{-C}_4\text{H}_9$	1A, a, b	109
$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2$	1A, a	109
$(\text{CH}_3)_3\text{CHCH}_2$	1A, a, b	108
$\text{C}_6\text{H}_5\text{CH}_2$	1A, a, b, d	32, 74, 109, 110
$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2$	1A, a	105
$\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{CH}_2$	1A, a	108
$p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2$	1A, a	105
cyclo- C_3H_5	1A, a	105
$\text{CH}_2=\text{CH}$	1B, a, d	109
$\text{CH}_3\text{CH}=\text{CH}_2$	1B	105
$\text{CH}_2=\text{CHCH}_2$	1A, a, b	109-111
$\text{CH}_3\text{CH}=\text{CHCH}_2$	1A, 1B, a, b	108-111
$\text{CH}_2=\text{C}=\text{CH}$	1A, a	105
$\text{C}_6\text{H}_5\text{CH}=\text{CH}$	1B	105
$\text{CH}_2=\text{CH}(\text{C}_6\text{H}_5)$	1B, a, b	105
$\text{Co}-\text{CH}=\text{CH}-\text{Co}$	a, b, d (see Section IV,C,2)	70
$\text{CH}\equiv\text{C}$	a (structure not established, see Section IV,C,2)	105
C_6H_5	1A (from $\text{C}_6\text{H}_5\text{N}_2\text{Cl}$), a	110
ClCH_2CH_2	1A, a	105

TABLE III *continued*

28. Pentacyanide Complexes

R	Prep. and characterization	References
ICH ₂ CH ₂	1A, a	32
ICH ₂ CH ₂ CH ₂	1A, a	32
ICH ₂ (CH ₂) ₂ CH ₂	1A, a	32
ICH ₂ (CH ₂) ₃ CH ₂	1A, a	32
<i>p</i> -BrC ₆ H ₄ CH ₂	1A	32
<i>p</i> -NO ₂ C ₆ H ₄ CH ₂	1A	32
HOCH ₂ CH ₂	1A, a, b	105
HOCH ₂ CH=CHCH ₂	1A, a	105
C ₂ H ₅ OCH ₂ CH ₂	1A, a	105
(C ₂ H ₅ O) ₂ CHCH ₂	1A, a	105
<i>p</i> -CH ₃ OC ₆ H ₄ CH ₂	1A, a	105
<i>p</i> -CH ₃ OCH ₂ C ₆ H ₄ CH ₂	1A, a	105
NCCH ₂	1A, a, b, d	109
NCCH ₂ CH ₂	1A, a, b, d	105
NCCH(CH ₃)	1A, 1B, a, b, d	108-110
NCC(CH ₃) ₂	1A, 1B, a, b	108
NCCH(C ₆ H ₅)	1A, a, b	108
NCCH(C ₂ H ₅)	1B, a	105
NCCH(CH ₂ C ₆ H ₅)	1B, a	105
1-NC-cyclo-C ₆ H ₁₀	1B, a, b	105
<i>p</i> -NCC ₆ H ₄ CH(CH ₃)	1B, a	108
CH ₃ COCH ₂	1A, a	105
CH ₃ COCH(CH ₃)	1A, 1B, a, b	105
C ₆ H ₅ COCH ₂	1A, a, b, d	109, 110
C ₆ H ₅ COCH(CH ₃)	1A, 1B, a, b	109, 110
Oxonorbornyl	1B, a, c	105
NH ₂ COCH ₂	1A, a	75
ÖOCCH ₂	1A, a, b	75
ÖOCCH(CH ₃)	1A, 1B, a, b	75, 105
ÖOCCH(CH ₂ COÖ)	1A, a	75
ÖOCCH ₂ CH ₂	1A, a	75
<i>p</i> -ÖOCC ₆ H ₄ CH ₂	1A, a	75
ÖOCCH=C(C ₆ H ₅)	1B, a, b	105
ÖOCCHDCH(COÖ)	1B, b	94
ÖOCCH(CHDCH ₃)	1B, b	94
CH ₃ OOCCH ₂	1A, a	75
CH ₃ OOCCH(CH ₃)	1A, 1B, a, b	105
CH ₃ OOCCH ₂ CH ₂	1A, a, b	75, 105
CH ₃ OOCCH(CH ₃) ₂	1B, a	105, 108
ROOCCH ₂ CH(COOR)	1B, a	105
C ₅ H ₄ NCH ₂	ortho-1A, b, c, d; meta-1A, b, c, d; para-1A, a, b, c, d	100, 101

TABLE III *continued*

28. Pentacyanide Complexes

R	Prep. and characterization	References
$C_5H_4NH^+CH_2$	ortho-1A, a, b, c; meta-1A, a, b, c; para-1A, a, b, c	100, 101
$C_5H_4N(CHCH_3)$	ortho-1A, 1B, a, c	102, 105, 108
$C_5H_4NH^+(CHCH_3)$	ortho-1A, c	102
$C_5H_4N^+$	ortho-1A, a, b, c, d	75
$C_5H_4NH^+$	ortho-1A	9
HCF_2CF_2	1B, a, b, d (see Section IV,C,2)	120-122
$Co-CF_2CF_2-Co$	a, b, d (see Section IV,C,2)	121, 122
$Co-C-S-Co$ S	2, a, c, d (see Section IV,C,2)	5, 125

29. Other Cyanide Complexes

Complex	Prep. and characterization	References
$[CH_3Co(CN)_4(CNH)]^{2-}$	4, c	101
$[CH_3CCo(CN)_4]^{2-}$ NH	4, b, c	101
$[CH_3CCo(CN)_4]^{2-}$ O	4, b, c	101
$[C_5H_4NHCH_2Co(CN)_4(CNH)]^-$	ortho-4, b, c; meta-4, b, c; para-4, b, c	101
$[C_5H_4NH^+CH_2Co(CN)_4(H_2O)]^-$	ortho-4, a, b, c; meta-4, a, b, c; para-4, c	101
$[C_5H_4NHCH_2CCo(CN)_4]^-$ NH	ortho-4, a, b, c, d; meta-4, a, b, c, d; para-4, a, b, c, d	101
$[C_5H_4NH^+CH_2CCo(CN)_4]^-$ O	ortho-4, c; meta-4, c; para-4, c	101
$[C_5H_4NH^+CHCH(CH_3)Co(CN)_4(H_2O)]^-$	ortho-4	102
$[C_5H_4NHCH(CH_3)Co(CN)_4(CNH)]^-$	ortho-4, c	102
$[C_5H_4NHCH(CH_3)CCo(CN)_4]^-$ NH	ortho-4, c, d	102
$C_5H_4NH^+CHCH(CH_3)CCo(CN)_3(CNH)$ NH	ortho-4	102

A. Corrinoids

Corrinoid complexes are almost exclusively cobalamins (in aqueous solution) carrying H-bonding amide side chains. The most common method of preparation is the reaction of the Co(I) derivative with electrophilic reagents, usually alkyl or substituted alkyl halides. Substitution of the axial ligand, X, in solution has been carried out to prepare complexes with a wide range of axial substituents, e.g., CN^- , imidazole, N_3^- . The Grignard route represents a fairly minor method of synthesis for these compounds. After the alkylation has been carried out, the organocobalt(III) complexes are extracted, usually from aqueous media into a phenol–chloroform solution. This separates inorganic impurities from the corrinoid complexes. The organo-corrinoids are then displaced back into aqueous solution again by the addition of acetone to the phenol–chloroform mixture. Chromatographic techniques including paper, thin-layer and ion-exchange methods are then used to separate the corrinoids from each other. Where there are mixtures of complexes present which differ only in the number of carboxylic acid side chains, electrophoresis may be used. The corrinoids may be removed from aqueous solution by freeze-drying, provided the axial ligand is stable to substitution. The solid material obtained, however, is not crystalline.

It is not possible unequivocally to establish the structure of a corrinoid by methods such as nuclear magnetic resonance, infrared spectroscopy, or elemental analysis because these molecules are so complex that spectra cannot be definitively interpreted and assigned, and chemical analysis would, for example, not detect with certainty an organocobalt methyl group in the presence of such a large amount of carbon and hydrogen in the complex. Paper and thin-layer chromatography are often used to establish the identity of an unknown corrinoid by comparison with a known one. X-ray analysis is the only absolute method for these compounds, and comparison through UV–visible spectra or reactivity with known structures often is the best approach possible (136). Occasionally spectroscopic methods may give a more positive identification than usual; e.g., the infrared spectrum can provide evidence for the presence of the $\text{HC}\equiv\text{C}$ moiety (97). The presence of the grouping CH_3Co or $\text{C}_2\text{H}_5\text{Co}$ can be proved fairly simply by NMR spectroscopy (88, 35, 20).

The most convenient route for introducing organo-ligands which do not contain strongly nucleophilic groups (e.g., $-\text{SH}$ or $-\text{NH}_2$), is from the organic halide (Section 1,a, below); in most cases $-\text{SH}$ and $-\text{NH}_2$ groups

may be prepared by ring-opening reactions. These ring-opening reactions offer interesting possibilities of synthesizing organocorrinoid derivatives not accessible by other routes. So far these opportunities have been little explored.

For a detailed list of references see ref. (136).

1. *Nucleophilic Attack by Co(I)*

a. *Substitution.* The alkylation is usually carried out by reduction of a cobalt(III) species to cobalt(I) using, e.g., sodium borohydride, or zinc and acetic acid or NH_4Cl . These reagents convert the *red* cobalt(III) complexes to the *green* cobalt(I) species. The cobalt(III) species may be B_{12} , B_{12a} (the hydroxy derivative) or cyano(aquo)cobinamide. The cobalt(I) species is then treated with the alkylating agent in the presence of an excess of the reducing agent. The alkylation can be easily followed by noting the color change from green to red and is usually rapid. The yields vary from almost quantitative to quite low because of continued reaction. Some organic ligands (e.g., $\text{HC}\equiv\text{C}$, CF_3CH_2 , and HO_3SCH_2) are cleaved by borohydride, and so this reducing agent should in these cases be replaced, e.g., by Cr(II) . Other problems have included alkylation on the side of the cobalt ring system where benzimidazole is usually coordinated, producing the 1-isomer rather than the normal u-isomer (see Section II,B,3). In addition, the electrophilic reagent may react in more than one way, e.g., bromoacetylene may give $\text{CoC}\equiv\text{CH}$ or $\text{CoCH}=\text{CHBr}$ (97).

Details of the organic groups which have been attached to cobalt in this way are given in Table III, 1. Almost all the work has been done with the cobalamins, but there is probably little difference in the behavior of $[\text{Co}^{\text{I}}(\text{cobin})]^-$ and $[\text{Co}^{\text{I}}(\text{cobal})]^-$. The Table includes only those examples where there is some definite evidence of an organocobalt(III) species. We have not included references to reagents reported *not* to react with $[\text{Co}^{\text{I}}(\text{corrin})]^-$ because in many cases this simply means that no organometallic species have been *detected*. It does not necessarily mean that no reaction has taken place. The usual alkylating agents include organic halides, carboxylates, sulfates, and tosylates. Diazomethane and trialkylsulfide derivatives have also been used. No reaction has been detected with tertiary halides, aromatic halides, or fluorocarbons such as CHF_3 .

b. *Addition to Unsaturated Compounds.* $[\text{Co}^{\text{I}}(\text{corrin})]^-$ will add to olefins which are activated by various substituents (e.g., fluorine atoms, or carboxylic acid groups), to acetylene, and to substituted acetylenes which are not

obstructed by bulky substituents at each end (e.g., $\text{C}_6\text{H}_5\text{C}\equiv\text{CCOOH}$). Details of organocobalt(III) compounds formed by this route are given in Table III,1.

2. *Reactions Involving Co(II)*

This process has not been used for preparative purposes. The mechanistic implications are discussed in Section III,B.

3. *Nucleophilic Attack on Co(III)*

A methyl group can be placed on cobalt in dicyano[cobyrinic acid heptamethyl ester] when it is treated with excess methyl magnesium iodide (the ester side chains being converted into tertiary alcohol groups). The alkylation could also be achieved using lithium alkyls (176). Presumably this reaction would be successful with any corrinoid which is soluble in solvents compatible with Grignard reagents.

4. *Other Reactions*

Methyl iodide will react with vitamin $\text{B}_{12\text{a}}$ in the presence of thiols or sulfide to produce methylcobalamin (56).

B. *Other Macrocyclic Complexes*

1. *Nucleophilic Attack by Co(I)*

a. *Substitution.* The Co^{I} complex is usually generated by reduction of complexes of the type $[\text{Co}^{\text{III}}(\text{L}_4)\text{BX}]$ $[\text{Co}^{\text{III}}(\text{L}_4)\text{B}_2]$ or $[\text{Co}^{\text{II}}(\text{L}_4)]$ (where B may be Ph_3P or pyridine, and X may be a halide ion usually bromide) (43, 40). $[\text{CH}_3\text{Co}(\text{salen})]$ has been reduced by sodium amalgam or Grignard reagent to $[\text{Co}^{\text{I}}(\text{salen})]^-$ (64). $[\text{Co}^{\text{III}}(\text{salen})\text{I}]$ can be reduced by a fourfold excess of Grignard reagent to yield $\text{MgX}^+[\text{Co}^{\text{I}}(\text{salen})]^-$, but $[\text{Co}^{\text{II}}(\text{salen})]$ may be reduced to the above derivative using only equimolar quantities of Grignard reagent (64, 26). Using $[\text{Co}^{\text{II}}(\text{salen})]$ it was found that longer reaction times and excess sodium amalgam caused the addition of a second electron to the system, producing an isolable disodium derivative (64). Reduction of $[\text{Co}^{\text{III}}(\text{porph})\text{pyBr}]$ using Adams catalyst produced only the Co^{II} derivative (96), but it was eventually found possible to reduce $[\text{Co}^{\text{II}}(\text{porph})]$ to $[\text{Co}^{\text{I}}(\text{porph})]^-$ using 15% sodium amalgam (33). Compounds of the neutral ligand CR, $[\text{Co}^{\text{II}}(\text{CR})\text{Br}_2]$ and $[\text{CH}_3\text{Co}(\text{CR})\text{Br}]^+$ may be reduced to $[\text{Co}^{\text{I}}(\text{CR})\text{Br}]^\circ$ and $[\text{CH}_3\text{Co}^{\text{I}}(\text{CR})]$, respectively, using

sodium borohydride in methanol or, preferably, sodium amalgam in acetonitrile (60, 130). Complexes of the uninegative ligand (DO)(DOH)pn may be reduced by sodium borohydride in methanol–water to give Co^{I} species (characterized by their *blue* color), e.g., $[\text{Co}\{(\text{DO})(\text{DOH})\text{pn}\}\text{X}_2]$ is reduced to $[\text{Co}^{\text{I}}\{(\text{DO})(\text{DOH})\text{pn}\}]$ (46). Reduction of $[\text{RCo}\{(\text{DO})(\text{DOH})\text{pn}\}\text{I}]$ by carbon monoxide in aqueous alkaline tetrahydrofuran produces a *green* cobalt(I) species, which reacts with alkyl halides to produce *trans*- $[\text{R}_2\text{Co}\{(\text{DO})(\text{DOH})\text{pn}\}]$ (42). It appears that the reduced species still has the original alkyl group attached to the cobalt atom; reduction of $[\text{C}_6\text{H}_5\text{Co}\{(\text{DO})(\text{DOH})\text{pn}\}]$ in the presence of CH_3I produces $[\text{C}_6\text{H}_5(\text{CH}_3)\text{Co}\{(\text{DO})(\text{DOH})\text{pn}\}]$, a mixed-ligand complex. $[\text{Co}^{\text{II}}(\text{phthal})]$ can be reduced to the Co^{I} derivative by an excess of dilithium benzophenone in tetrahydrofuran (174), and its solution in dimethylacetamide containing 2½% pyridine can also be reduced by hydrazine, sodium borohydride, or sodium sulfide (54). Aqueous solutions of $[\text{Co}^{\text{II}}(\text{phthalTS})]$ can be reduced by borohydride, hydrazine, sodium sulfide, cysteine, zinc, and titanium(III) ions (25, 54, 104).

In work on DMG complexes NaBH_4 has been much used. Reduction of $\text{Co}(\text{II})$ derivatives is usually the most convenient route as they may be formed and reduced *in situ*, e.g., a suspension of DMG and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (2:1 molar ratio) in methanol is stirred to dissolve the cobalt chloride. Then 50% NaOH (2:1 molar ratio of NaOH to CoCl_2) and pyridine (equimolar amounts to $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) was added, and the stirred suspension cooled to -10°C , followed by addition of more 50% NaOH and NaBH_4 (1:6 mole ratio of NaBH_4 to $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$). At this point the alkylating agent (Me_2SO_4) was added and the solution warmed to room temperature. Evaporation and addition of water and pyridine produces a solid crystalline product in 74% yield (161). The $\text{Co}(\text{I})$ derivatives are usually blue-green, whereas the organocobalt(III) compounds are yellow to red. This color change is a useful indication as to the progress of the reaction. Molecular hydrogen has been used as a reducing agent for reactions of DMG complexes. Again this may be carried out in a one-step process e.g., treatment of a suspension of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and DMG in methanol with the appropriate amount of sodium hydroxide and the alkylating agent in the presence of hydrogen produces the alkyl cobalt(III) derivatives. This illustrates the general ease of reduction of DMG complexes; porphyrin or corrinoid systems are not reduced to cobalt(I) derivatives by this method. In fact, $[\text{Co}^{\text{II}}(\text{DMG})_2]$ disproportionates into cobalt(I) and (III) in alkaline solution.

Addition of sodium hydroxide to a mixture of $[\text{Co}^{\text{II}}(\text{DMG})_2]$ and an alkylating agent in methanol-water yields up to 50% of the organocobalt product. This appears to be the most convenient method for the preparation of organocobalt(III) derivatives, provided that the maximum yield is not required (161, 163). Methods involving the reaction of Co^{I} with electrophiles are, at least with DMG complexes, more convenient than the main alternative route via $\text{Co}(\text{III})$ and Grignard reagents.

The $\text{Co}(\text{I})$ complexes may be treated with a variety of electrophilic reagents, usually the alkyl bromide or iodide. The alkyl group may be primary or secondary [tertiary alkyl halides do not give isolable products (153)], benzyl, allyl [but the products were too reactive to isolate (130, 131, 162)] or cycloalkyl (147, 154). With dihalides mono- or dicobalt derivatives may be formed depending on the proportions of the reagent or the reaction time (40, 161). Examples of other halides are acyl chlorides, haloesters such as ClCOOCH_3 (43), $\text{BrCH}_2\text{CH}_2\text{OH}$ (33, 34), BrCH_2COPh (163), and vinyl and styryl halides (43, 59, 129, 163). Other methylating and alkylating agents include CH_2N_2 (151), Me_2SO_4 (161), and tosylates (95, 155). Reaction with phenyl halides has apparently been achieved only with $[\text{Co}^{\text{I}}(\text{BAE})]^-$ (16, 46).

Certain quaternary ammonium salts will alkylate $[\text{Co}^{\text{I}}(\text{DMG})_2\text{py}]^-$. The addition of $\text{PhCH}_2\text{NMe}_3^+\text{I}^-$ to a solution of the complex in methanol gives the PhCH_2Co complex in 45% yield. The reaction works more slowly with dimethylpiperidinium iodide to give the $\text{CH}_3\text{—Co}$ complex (15). There is no alkylation with tertiary amines alone (164), but in the presence of equimolar amounts of dimethylacetylenedicarboxylate certain aliphatic tertiary amines can alkylate $[\text{Co}^{\text{I}}(\text{DMG})_2\text{py}]^-$ in methanol solution. The reaction also produces the enamine derivative of a maleic ester, and the mechanism appears to involve addition of the amine to the triple bond to form an ammonium salt, which can then attack the $\text{Co}(\text{I})$ derivative (15).

b. *Addition to Unsaturated Compounds.* Of the simple alkyl olefins only propylene will react with $[\text{Co}^{\text{I}}(\text{DMG})_2\text{py}]^-$, to give small amounts of $[i\text{-PrCo}(\text{DMG})_2\text{py}]$ under special conditions, viz., reaction of $[\text{pyCo}(\text{DMG})_2]_2$ with excess propylene in ethanol in the presence of hydrogen (161). Addition to unsaturated derivatives is successful for acetylene and acetylenic derivatives, and for olefins possessing electron-attracting substituents, i.e., activated systems. The method of carrying out these reactions is, usually, to generate and reduce a $\text{Co}(\text{II})$ derivative *in situ*: $\text{Co}(\text{acetate})_2$ or $\text{Co}(\text{halide})_2$, DMG, and a solution of the olefinic substrate are stirred in methanol under 1 atm of H_2 . In neutral solution only α -

substituted organocobalt(III) DMG complexes are formed, but if NaOH is added (pH 10–11) the β -substituted complex is formed, e.g., with $\text{CH}_2=\text{CHCN}$ in neutral solution $[\text{CH}_3\text{CH}(\text{CN})\text{Co}(\text{DMG})_2\text{py}]$ is formed, but if NaOH is added $[\text{NCCH}_2\text{CH}_2\text{Co}(\text{DMG})_2\text{py}]$ results. The β -substituted derivatives are less stable than the α -substituted derivatives and may be converted to them (163). These reactions may still occur if hydrogen is omitted because of the disproportionation referred to above. The reaction product from styrene under both alkaline and neutral conditions is the α -phenylethyl derivative, not the β -product. The β -isomer has been made from β -bromoethylbenzene and is known to be stable. In these preparations the olefinic substrate is usually employed in excess to counteract losses through reductive cleavage of the cobalt–carbon bond. Only with highly reactive olefins is reduction of the organocobalt products insignificant enough to be neglected (163). As discussed in Section III, the direction of addition to the olefinic derivative is usually diagnostic of the nucleophile involved; α -substituted derivatives result from reactions with the cobalt hydride, β -substituted products arise from the Co^{I} nucleophile. The desired base ligand may be added before the hydrogenation stage (if used) or after the main reaction phase is over, prior to isolation of the organometallic complexes. This gives a wide choice of base ligands using convenient reaction conditions (163). Hydride derivatives $[\text{HCoL}_4]^{\circ}$ have also been prepared for (salen) and (BAE) systems. These react with acetylenes to give vinyl complexes and with activated olefins to give saturated organocobalt complexes (43, 40).

Aniline and formaldehyde in water added to $[\text{Co}^{\text{II}}(\text{DMG})_2(\text{H}_2\text{O})_2]$ in methanol under 1 atm of hydrogen produces, on addition of water, a precipitate which may be $[\text{C}_6\text{H}_5\text{NHCH}_2\text{Co}(\text{DMG})_2(\text{NH}_2\text{C}_6\text{H}_5)]\text{H}_2\text{O}$ (165).

2. Reactions Involving $\text{Co}(\text{II})$

a. *Radicals and $\text{Co}(\text{II})$.* Various complexes of the type $[\text{Co}^{\text{II}}(\text{DMG})_2\text{B}]$, $[\text{Co}^{\text{II}}(\text{DMG})_2\text{B}_2]$, and $[\text{Co}^{\text{II}}(\text{saloph})\text{B}]$ were found to react with benzyl halides in benzene or acetone (no base being added to make the solutions alkaline) to yield $[\text{PhCH}_2\text{Co}(\text{DMG})_2\text{B}]$ and $[\text{XCo}^{\text{III}}(\text{DMG})_2\text{B}]$. The mechanism has been discussed in Section III, B (119, 144). Few complexes have been isolated from this preparative route; analytical results have been obtained for $[\text{C}_6\text{H}_5\text{CH}_2\text{Co}(\text{saloph})\text{pyH}_2\text{O}]$ (119, 144).

b. *Electron-Transfer Reactions.* This is successful only when strongly electron-attracting groups are present in an alkyl halide. It has been observed only for $p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2$ halides and differs from the reactions discussed

above (2,a) in that electron transfer rather than halogen abstraction occurs (118). The process is exemplified by the reaction of $[\text{Co}^{\text{II}}(\text{salen})\text{MeIMD}]$ with $p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{Br}$ which proceeds quantitatively (giving 50% of the metal-organic derivative) in CH_2Cl_2 solution in the presence of excess methylimidazole. However, the organocobalt(III) complexes were not isolated as solids or analyzed, and the method cannot be considered as a practical means of synthesizing organometallic derivatives but has interest because of its mechanistic implications (see also Section III,B).

3. Reactions Involving Co(III)

a. *Nucleophilic Attack on Co(III)*. Reaction of $[\text{Co}^{\text{III}}(\text{salen})\text{B}_2]^+$, $[\text{Co}^{\text{III}}(\text{salen})\text{BX}]$ (47), or $[\text{Co}^{\text{III}}(\text{salen})\text{I}]$ (64) with excess (47) or equivalent (64) amounts of Grignard reagent yields $[\text{RCo}(\text{salen})\text{H}_2\text{O}]$ no matter which base, B, was originally attached to the cobalt(III) compound. The reaction with $[\text{Co}^{\text{III}}(\text{salen})\text{I}]$ appears to be the simplest and least complicated by the presence of other ligands and does not require an excess of Grignard reagent. Similarly with $[\text{Co}^{\text{III}}(\text{BAE})\text{BX}]$ the base Ph_3P is not retained after attack by R^- [e.g., from $\text{C}_6\text{H}_5\text{Li}$ or $\text{C}_6\text{H}_5\text{MgBr}$ in the case of phenyl] (49). R^- may also originate from $[(\text{CH}_3)_2\text{Co}\{(\text{DO})(\text{DOH})\text{pn}\}]$ which can react in water/THF solution at room temperature with $[\text{Co}^{\text{III}}\text{L}_4(\text{H}_2\text{O})_2]$, where $\text{L}_4 = \text{BAE}$, salen, saloph, or $(\text{DOH})(\text{DO})\text{pn}$, to form the methylcobalt(III) derivative in 70–90% yields (41). The reaction of $[\text{Co}^{\text{III}}(\text{porph})\text{pyBr}]$ with Grignard reagents yields $[\text{RCo}(\text{porph})\text{H}_2\text{O}]$ (56, 33). Reaction of $[\text{Co}^{\text{III}}(\text{DMG})_2\text{BX}]$ with Grignard reagents requires a threefold excess of the nucleophile because of the acidity of the two oxime protons (146). The Grignard route is the only practical one for phenyl halides, except with BAE complexes. Reaction of $[\text{Co}^{\text{III}}(\text{DMG})_2\text{pyCl}]$ with PhMgBr gives $[\text{PhCo}(\text{DMG})_2\text{py}]$ the base being retained as the sixth axial ligand (146). Though the Grignard route was the original method for the preparation of organocobalt(III) DMG complexes (151), it is less used now, mainly because Co(II) derivatives are more convenient starting materials (161). Using cobalt(II) starting materials eliminates the necessity of synthesizing a $[\text{Co}^{\text{II}}(\text{L}_4)]$ derivative in a separate step, and the experimental conditions are more convenient than for Grignard reactions. Reaction of $[\text{Co}^{\text{III}}\{(\text{DO})(\text{DOH})\text{pn}\}_2\text{I}_2]$ with a 2:1 excess of Grignard reagent gives $[\text{RCo}\{(\text{DO})(\text{DOH})\text{pn}\}]^+$; reaction with a (presumably greater) excess of Grignard reagent gives $[\text{R}_2\text{Co}\{(\text{DO})(\text{DOH})\text{pn}\}]$ (46, 42). Electrochemical reduction of $[\text{RCo}\{(\text{DO})(\text{DOH})\text{pn}\}\text{H}_2\text{O}]^+$ (where $\text{R} = \text{CH}_3$ or C_2H_5) generates

$[\text{RCo}^{\text{I}}\{(\text{DO})(\text{DOH})\text{pn}\}]^-$ which reacts with the parent species to give $[\text{R}_2\text{Co}^{\text{III}}\{(\text{DO})(\text{DOH})\text{pn}\}]$, presumably by release of the organic group as a carbanion (50). The Grignard method is normally carried out in tetrahydrofuran solution, a solid product being obtained by removal of THF in vacuum. The solid can be dissolved in methanol and precipitated with water. This method produces a complex having water in the sixth coordination position.

The reaction of $[\{\text{Co}^{\text{II}}(\text{DMG})_2\text{py}\}_2]$ with $\text{B}(n\text{-C}_4\text{H}_9)_3$ in benzene followed by extraction with $\text{CH}_2\text{Cl}_2/\text{aq. NaOH}$ produces $[n\text{-BuCo}(\text{DMG})_2\text{py}]$; the reaction is less successful with $[\text{pyCo}^{\text{III}}(\text{DMG})_2\text{Cl}]$ (161). This may be a convenient method using the more stable arylboron derivatives, but is probably experimentally more difficult than the Grignard route if a lower alkyl is to be introduced, because the lower alkylboron compounds inflame spontaneously in air, though they do not react with water, while the aryls are stable in air.

b. $[\text{ROCo}^{\text{III}}(\text{L}_4)\text{B}]$ and Active Hydrogen Compounds. The electrophilic behavior of the $\text{Co}(\text{III})$ species is shown by the reaction of $[\text{HOCO}^{\text{III}}(\text{L}_4)\text{H}_2\text{O}]$, where $\text{L}_4 = \text{salen}$, 7-Me-salen, saloph, $(\text{DMG})_2$, or $(\text{DO})(\text{DOH})\text{pn}$, with compounds such as acetone and nitromethane which contain an active hydrogen, for example, $[\text{HOCO}^{\text{III}}(\text{salen})\text{H}_2\text{O}] + \text{CH}_3\text{NO}_2 \rightarrow [\text{NO}_2\text{CH}_2\text{Co}(\text{salen})\text{H}_2\text{O}] + \text{H}_2\text{O}$. The hydroxo-cobalt(III) complex is dissolved in methanol or 9:1 methanol:water and reacted directly with the active hydrogen compound (16). Malononitrile, $\text{CH}_2(\text{CN})_2$, will also react with $[\text{ROCo}^{\text{III}}(\text{salen})]$, $[\text{HOCO}^{\text{III}}(\text{salen})\text{py}]$, and $[\text{CH}_3\text{OCO}^{\text{III}}(\text{salpn-1,3})]$, to give the $(\text{NC})_2\text{CHCo}$ derivatives. The reaction can also be carried out with $\text{Co}^{\text{II}}(\text{salen})$, oxygen, and $\text{CH}_2(\text{CN})_2$ in ethanol to produce polymeric $[(\text{NC})_2\text{CHCo}(\text{salen})]$, which gives the pyridine or aquo adduct on treatment with pyridine or aqueous acetone, respectively (4).

Experimentally, this method appears to be one of the most simple and convenient yet devised for the production of organocobalt(III) complexes. It would seem to be general for most equatorial ligands, the limiting factor being the requirement that the precursor of the organo-ligand must be an active hydrogen compound.

4. Preparations from Other Organocobalt(III) Compounds

a. *Addition, Exchange, or Removal of an Axial Ligand.* This reaction is frequently used to prepare organocobalt(III) complexes with different ligands (usually neutral bases) in the sixth coordination position. The

complexes $[\text{RCo}(\text{L}_4)\text{py}]$ ($\text{R} = \text{Me, Et, Pr, etc.}, \text{L}_4 = \text{salen or BAE}$) may be obtained by dissolving the aquo or anhydrous derivative in the minimum amount of pyridine and precipitating with petroleum ether (90% yield) (40). Ammonia derivatives may be obtained by bubbling ammonia gas into a solution of the aquo or anhydrous derivative; ether or light petrol is added to precipitate the product (47). Benzimidazole can be coordinated by pouring a solution of the ligand in methanol into a solution of the aquo derivative in methanol; after standing the benzimidazole derivative crystallizes out of solution (47). The compound $[\text{CH}_3\text{Co}(\text{DMG})_2\text{H}_2\text{O}]$ is best prepared from $[\text{CH}_3\text{Co}(\text{DMG})_2(\text{Me}_2\text{S})]$ by boiling the latter in water; on standing the liquid is filtered to obtain orange crystals of the aquo derivative. This compound can also be made from $\text{Co}^{\text{II}}(\text{DMG})_2$, hydrogen and methyl iodide in alkaline solution, but isolation is difficult, hence the indirect method from the Me_2S derivative (161, 146).

Five-coordinate complexes may sometimes arise spontaneously during preparation, e.g., $[\text{CH}_3\text{COCO}(\text{salen})]$ from CH_3COCl and $[\text{Co}^{\text{I}}(\text{salen})]^-$ (43) and $[\text{EtCo}(\text{salen})]$ from $[\text{Co}^{\text{III}}(\text{salen})(\text{NH}_3)_2]^+\text{Br}$ and EtMgBr , even though water was used at the recrystallization stage (47). But usually the five-coordinate complex has to be formed by removal of the sixth ligand (see also Section II, B, 1). This may be done by heating the aquo derivatives at $40^\circ\text{--}80^\circ\text{C}$ under vacuum in the solid state. There is usually a color change from the red-orange aquo derivative to a green anhydrous complex, though $[\text{CH}_2=\text{CHCo}(\text{salen})]$ is violet (40). It should be noted that $[\text{CH}_3\text{Co}(\text{salen})]$ has both red and green forms. The *green* derivative was obtained by dehydration of the aquo derivative over P_2O_5 *in vacuo* in darkness; the *red* derivative was obtained from the green compound by treatment with anhydrous diethyl ether, followed by filtration and drying *in vacuo* (64). $[\text{CH}_3\text{Co}(\text{DMG})_2\text{H}_2\text{O}]$ can be dehydrated by distilling from benzene or methylcyclohexane solution until the distillate is no longer moist. The material collected, washed with benzene, and dried at 25°C was the anhydrous $[\text{CH}_3\text{Co}(\text{DMG})_2]$ (161).

The pyridine ligand in some alkenyl cobalt(III) DMG complexes may be replaced by methyl or ethyl phosphite by addition of the phosphite to a solution of the $(\text{DMG})_2$ complex in ethanol. In a similar manner aniline may be displaced by $(\text{CH}_3\text{O})_3\text{P}$ from $[\text{CH}_2=\text{CHCo}(\text{DMG})_2\text{C}_6\text{H}_5\text{NH}_2]$ (129).

b. *Modification of the Organo-Ligand.* Acid hydrolysis has been used to obtain complexes such as $[\text{HOOCCH}_2\text{CH}_2\text{Co}(\text{DMG})_2\text{py}]$ from the methyl ester and $[\text{OHCCH}_2\text{Co}(\text{DMG})_2\text{py}]$ from the acetal (163). The aquation of

ethynylcobalamin ($\text{HC}\equiv\text{CCo}$) in aqueous acid gives acetylcobalamin ($\text{CH}_3\text{-COCo}$) (77), and that of the allenyl complex $[\text{CH}_2=\text{C}=\text{CHCo}(\text{DMG})_2\text{py}]$ in aqueous methanolic HCl gives the acetonyl complex ($\text{CH}_3\text{COCH}_2\text{Co}$) (99). The reaction of $[\text{CH}_3\text{Co}(\text{CN})_5]^{3-}$ with acid yields $[\text{CH}_3\text{C}(=\text{NH})\text{Co}(\text{CN})_4]^{2-}$, which then decomposes to a compound believed to be $[\text{CH}_3\text{COCO}(\text{CN})_4]^{2-}$ (101) (see also Section VI,D).

The reaction of $[\text{CH}_3\text{Co}(\text{salen})\text{H}_2\text{O}]$ with $n\text{-C}_3\text{F}_7\text{I}$ results in the formation of $[n\text{-C}_3\text{F}_7\text{Co}(\text{salen})]$ in almost quantitative yield. The reaction occurs in 3 days at room temperature or within 30 minutes on refluxing in ethylene glycol dimethyl ether (174a).

c. *Modification of the Equatorial Ligand.* The bridging protons in DMG complexes can be replaced by $-\text{BF}_2-$ bridging groups by, for example, stirring $[\text{CH}_3\text{Co}(\text{DMG})_2\text{py}]$ and $\text{Et}_2\text{O}\cdot\text{BF}_3$ together in ether and adding excess pyridine (71% yield) (161). The $(\text{DMG})_2$ ligand can be replaced by $(\text{CHD})_2$ by heating a suspension of $[\text{CH}_3\text{Co}(\text{DMG})_2\text{H}_2\text{O}]$ and cyclohexanedione dioxime in toluene for 4 hours at 135°C . The product is obtained as $[\text{CH}_3\text{Co}(\text{CHD})_2\text{py}]$ by concentrating the reaction mixture to dryness, and adding pyridine in methanolic sodium hydroxide. Water is then added to the mixture to precipitate the solid product (59% yield) (161).

The reaction of $[\text{RCo}(\text{BAE})]$ where $\text{R} = \text{Me}$ or Et with $[\text{Co}^{\text{II}}(\text{tfen})]$ in dimethyl sulfoxide gives $[\text{RCo}(\text{tfen})]$ (174a) (see also Section VI,C,3).

d. *Reaction of $[\text{RCo}(\text{L}_4)\text{H}_2\text{O}]$ with O_2 and CO in $\text{R}'\text{OH}$ to give $[\text{R}'\text{OCOCO}(\text{L}_4)\text{H}_2\text{O}]$.* Irradiation of the compounds $[\text{RCo}(\text{salen})\text{H}_2\text{O}]$ ($\text{R} = \text{Me}, \text{Et}, n\text{-Pr}, n\text{-Bu}$) with visible or UV light in solution in alcohols $\text{R}'\text{OH}$ ($\text{R}' = \text{Me}, \text{Et}, i\text{-Pr}$) in the presence of CO and air gives $[\text{R}'\text{OCOCO}(\text{salen})\text{H}_2\text{O}]$ (44, 38). The reaction occurs in three stages: photoreduction of the organocobalt(III) complex to $\text{Co}(\text{II})$, followed by oxidation to $[\text{R}'\text{OCo}^{\text{III}}(\text{salen})\text{H}_2\text{O}]$, and finally insertion of CO to give the alkoxycarbonyl complex $(\text{R}'\text{OCOCO})$ (see also Section III,C). The reaction has been extended to complexes of ligands such as salpn-1,3 , 7-Ph-salen, saloph, and BAE. In these examples the starting material is $[\text{Co}^{\text{II}}(\text{L}_4)]$, which is oxidized to $[\text{ROCo}^{\text{III}}(\text{L}_4)\text{H}_2\text{O}]$ when a 50:50 mixture of CO and air is bubbled through the suspension; the alkoxycarbonyl complex is eventually precipitated and can be recrystallized from methanol and water. The complexes $[\text{CH}_3\text{OCo}^{\text{III}}(\text{L}_4)\text{X}]$ and $[\text{HOCO}^{\text{III}}(\text{L}_4)\text{X}]$ were prepared, but only the latter were isolated; solutions of these complexes in methanol all give quantitative yields of the alkoxy carbonyl complexes when treated with CO , even in the absence of oxygen (44). This interesting reaction is

obviously of restricted synthetic usefulness, though there appears to be no reason why it should not be applied more widely to the preparation of alkoxy carbonyl derivatives of a wider range of equatorial ligands.

C. Penta- and Tetracyanides

Few organopentacyanocobalt(III) complexes have been isolated pure, probably because of the difficulty of separating them from other complexes of the type $[\text{Co}(\text{CN})_5\text{X}]^{3-}$ where $\text{X} = \text{Cl}^-$, CN^- , HO^- , etc. (74). The organocobalt(III) derivatives are usually detected in the presence of such inorganic cyanide complexes by observation of a characteristic cyanide stretching frequency at about 2100 cm^{-1} , which is about 25 cm^{-1} lower than analogous bands in the purely inorganic complexes. NMR spectroscopy in D_2O is also used to identify the presence of organic groups bound to cobalt. The stability of these complexes varies with the nature of the organo-ligand in the order $\text{XCH}_2 > \text{XCHMe} > \text{XCM}_2$ and $\text{X} = \text{CN} > \text{COOR} > \text{COR} > \text{CH}=\text{CH}_2 \sim \text{R} > \text{C}_6\text{H}_5$, (108) (see also Table V). The methods of preparation and characterization of organopentacyanides are given in Table III, 28. The work involving organocobalt(III) pentacyanides has been carried out mainly in aqueous media, in which the ions are soluble. The main interest in these systems lies in the investigation of their activity as hydrogenation catalysts (see Section VII), and in the study of their reaction with organic halides (see Section III,B). Nearly all these complexes are pentacyanides, though a few tetracyanides are known. Some of the reactions may be varied to involve the presence of either $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ or $[\text{HCo}(\text{CN})_5]^{3-}$, e.g., the reaction with $\text{CF}_2=\text{CF}_2$ can be made to give, respectively, $[(\text{CN})_5\text{CoCF}_2\text{CF}_2\text{Co}(\text{CN})_5]^{6-}$ and $[\text{HCF}_2\text{CF}_2\text{Co}(\text{CN})_5]^{3-}$ (122, 121). The Grignard route used for corrinoids and other macrocycles cannot be used for the preparation of the cyanide complexes, because they are soluble only in protic solvents. The anion $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ is prepared by addition of excess cyanide to aqueous solutions of cobaltous salts in an inert atmosphere, and can be reduced to $[\text{HCo}(\text{CN})_5]^{3-}$ by H_2 , 3% potassium amalgam, borohydride, etc.

1. Reactions of $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ and $[\text{HCo}(\text{CN})_5]^{3-}$

a. *Reactions of $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ with Organic Halides.* The mechanism of this reaction has been discussed in Section III,B. Products are shown in Table III, 28.

Alkyl pentacyanides prepared by this reaction are usually obtained from primary alkyl iodides. Low yields of the iso- and cyclopropyl derivatives were isolated from the corresponding iodide and bromide. In general, secondary and tertiary alkyl iodides form mixtures of alkanes and alkenes, presumably because of the instability of the organometallic complexes (105, 109). Neopentyl and neophyl iodides yield unrearranged organocobalt complexes. The structures of complexes formed from polyhalogenated compounds such as CH_2Cl_2 and Cl_3CCOOH have not been determined. Benzyl halides give the expected organocobalt complexes, but $\text{C}_6\text{H}_5\text{CHMeBr}$ gives a mixture of $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$ and $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$ (105).

Allyl halides react to produce σ -allyl pentacyanide complexes, which can be converted into π -allyl complexes by displacement of a cyanide ligand (107, 109) (see also Section V,C). $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Br}$ gives a low yield of the 2-butenylcobalt complex (105). α -Cyanoalkyl halides and α -halo-ketones and acids give the corresponding organocobalt complexes. The only known tertiary complex, $[\text{Me}_2\text{C}(\text{CN})-\text{Co}(\text{CN})_5]^{3-}$, is presumably stabilized by the presence of the highly electronegative nitrile group (105). α -Iodopyridine is the only aromatic halide reported to react with $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ (75). The phenyl complex has been prepared from phenyldiazonium chloride (109).

b. *Reaction of $[\text{HCo}(\text{CN})_5]^{3-}$ with Conjugated Olefins.* Activated olefins may be catalytically hydrogenated, be isomerized, or form adducts by reaction with $[\text{HCo}(\text{CN})_5]^{3-}$, while nonactivated olefins are neither reduced nor isomerized; the direction of the reaction appears to be governed by the structures of the olefins (see Sections III,A and VII,A). Vinyl halides react in an addition-elimination reaction to give the vinyl complexes (see Section III,A). The organocobalt pentacyanides formed by these reactions are listed in Table III, Section 28.

2. Other Reactions

Acetylene reacts with $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ to form a bridged binuclear complex $[(\text{NC})_5\text{CoCH}=\text{CHCo}(\text{CN})_5]^{6-}$ (70). This complex rearranges in solution to give an organometallic complex (containing nitrile groups) whose structure is not known (105). The original bridged complex was obtained by passing acetylene gas into an air-free aqueous solution of hydrated cobalt(II) chloride and potassium cyanide which was cooled by ice. After a few minutes the color changed from green to yellow, and addition of air-free ethanol precipitated a yellow-brown oil which soon crystallized.

The crystals were washed with ethanol and ether and dried under vacuum (70).

C_2F_4 reacts with both $[HCo(CN)_5]^{3-}$ and $[Co(CN)_5]^{3-}$ to give, respectively, $[HCF_2CF_2Co(CN)_5]^{3-}$ and $[(CN)_5CoCF_2CF_2Co(CN)_5]^{6-}$. The reaction takes place in aqueous solutions at atmospheric pressure (122, 121). The presence of potassium amalgam in the former case produces $[HCo(CN)_5]^{3-}$ which gives almost exclusively the $HCF_2CF_2^-$ product. The complexes were isolated by precipitation with ethanol (121). The reaction of $[Co^{II}(CN)_5]^{3-}$ with CS_2 produces $[(NC)_5CoS-C \equiv Co(CN)_5]^{6-}$ (125, 5).



Reaction of (presumably) $[Co^{II}(CN)_5]^{3-}$ with $ClCH=CHCl$ is thought to produce $[Co(CN)_5C \equiv CH]^{3-}$ (105).

A series of complexes in which the cyanide ligands are modified or replaced arises from the decomposition of methyl and pyridiomethylcobalt(III) pentacyanide derivatives in acid solution. The reactions include protonation of a cyanide ligand, insertion of a cyanide ligand between the organic group and the cobalt atom to produce an imine (see Section VI, D), decomposition of this imine to an acyl product, and replacement of a cyanide ligand by water (100, 101). The products are listed in Table III, 29.

V

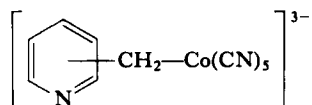
REACTIONS AND EQUILIBRIA NOT INVOLVING CLEAVAGE OF THE $Co-C$ BOND

A. Acid/Base Equilibria

Several organo-ligands can gain or lose a proton. The values of pK_a given in the accompanying tabulation have been reported for complexes of the type $[RCo(DMG)_2X]$ (163).

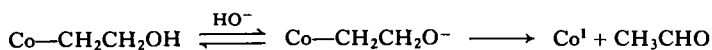
R =	X =	pK_a
$-CH_2CH_2COOH$	py	5.70
$-CHMeCOOH$	py	All apparently 7.14
$-CH_2COOH$	py	
$-CHMeCOOH$	H_2O	
cf. CH_3CH_2COOH		4.87

Values of pK_b have been determined for protonation of the pyridiomethyl ligand in all three isomers of the complexes

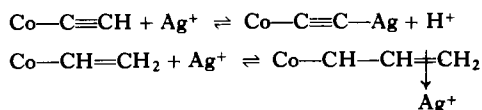


as follows: 2-pyridiomethyl, $pK_b = 10.4 \pm 0.1$; 3-, 8.3 ± 0.1 ; 4-, 9.2 ± 0.1 ; cf. 4-methylpyridine, 6.1. There is also protonation of one of the cyanides in strong acid (pK approx. -2) (101). The pK_b of the α -(2-pyridio)ethyl-pentacyanide is 10.55 (102).

Acid and base can, of course, induce many reactions of organocobalt(III) complexes (see Section B below, and Section VI, B, C, D), presumably through the formation of reactive intermediates by the gain or loss of a proton, e.g.,



Organo-ligands which can pick up a proton should also be able to act as Lewis bases towards metal ions, but only two cases have so far been reported. Ethynyl- and vinylcobalamin both show reversible equilibria with Ag(I) ions, which have been ascribed to equilibria such as



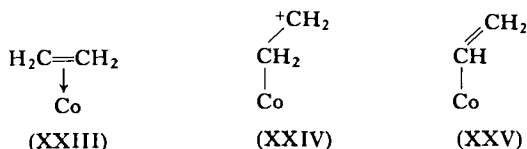
but no equilibrium constants have been reported (84). The complex $[\text{ClCH}_2\text{Co}(\text{DMG})_2\text{H}_2\text{O}]$ also forms a very strong adduct ($K \geq 5 \times 10^6 \text{ M}^{-1}$) of unknown structure (? $\text{CoCHCl}-\text{Hg}^+$) with Hg(II) ions (1).

NMR studies show no exchange of protons between solvent and organo-ligands [see, for example, ref. (161)].

B. Irreversible Reactions

A study of the reactions of the complexes $[\text{CH}_3\text{COOCHRCH}_2\text{Co}(\text{DMG})_2\text{py}]$, where R is H or CH_3 , shows that the β -carbon atom is unusually reactive. Hydrolysis gives alcohols ($\text{CoCH}_2\text{CHROH}$), while methanolysis

and ethanolysis give ethers ($\text{CoCH}_2\text{CHROR}'$). The kinetic data obtained for ethanolysis showed that these complexes possess a reactivity comparable to that of trityl acetate. They suggested the intermediate formation of a complex such as (XXIII) or (XXIV). The σ -vinyl complex (XXV) could be excluded because the products of alcoholysis in CD_3OD contained D

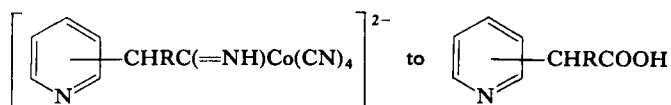


only in the methoxy group. The occurrence or otherwise of the redistribution of isotopic labeling between the α - and β -positions during the reaction could presumably decide between (XXIII) and (XXIV). These reactions are accompanied by some loss of the organo-ligand (presumably as olefin), and if hydrolysis is carried out in the presence of BH_4^- some of the *n*-propyl complex ($\text{CH}_3\text{CH}_2\text{CH}_2\text{Co}$) is also formed (69).

Such reactions occur far less readily at the α -carbon atom. The β -carbomethoxyethyl complex $[\text{MeOOCCH}_2\text{CH}_2\text{Co}(\text{DMG})_2\text{py}]$ is saponified by 1 *N* HCl, while the α -analog requires warm concentrated sulfuric acid, and the complex with the ligand $\text{EtOOCCH}_2\text{CH}(\text{COOEt})\text{Co}$ can be selectively hydrolyzed to give the α -monoester. It was suggested that the presence of the equatorial ligand severely hinders the approach of an attacking nucleophile to the carboxy group on the α -carbon (163). X-Ray analysis of $[\text{MeOOCCH}_2\text{Co}(\text{DMG})_2\text{py}]$ does, in fact, reveal steric compression between the carboxy carbon and one of the nitrogens of DMG (112) (see also Section II,B,2).

Many unsaturated organo-ligands undergo hydrolysis or hydration while remaining coordinated to the cobalt. The hydration of ethynylcobalamin ($\text{HC}\equiv\text{CCo}$) to acetylcobalamin (CH_3COCO) in aqueous acid was reported in 1965 (77). A second clear-cut example is the hydration of solutions of the σ -allenyl complex $[\text{CH}_2=\text{C}=\text{CHCo}(\text{DMG})_2\text{py}]$ in aqueous methanol to the acetyl complex ($\text{CH}_3\text{COCH}_2\text{Co}$) catalyzed by HCl (99). Phenylacetylene reacts with $[\text{Co}(\text{CN})_5\text{H}]^{3-}$ to give the α -styryl complex, which is decomposed by acid to yield acetophenone (PhCOCH_3), but the nature of the intermediate steps is not known (105). One product of the reaction of $[\text{CH}_3\text{Co}(\text{CN})_5]^{3-}$ with acid is $[\text{CH}_3\text{C}(=\text{NH})\text{Co}(\text{CN})_4]^{2-}$, which then yields ammonia and a product which is almost certainly the acetyl complex

$[\text{CH}_3\text{COC}(\text{CN})_4]^{2-}$ (101). The acid-catalyzed hydrolysis of other complexes of the type

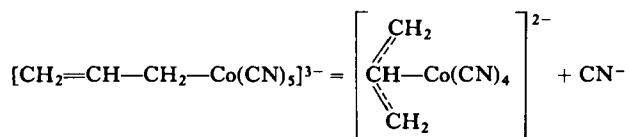


might also proceed via acylcobalt intermediates (101, 102). It is worth noting that cobalt cyanide complexes apparently catalyze the hydrolysis of nitriles (RCN) to carboxylic acids (RCOOH) (127).

C. σ - π Equilibria

Several types of reversible equilibria involving π -bonded organo-ligands have now been established and some play an important role as reaction intermediates.

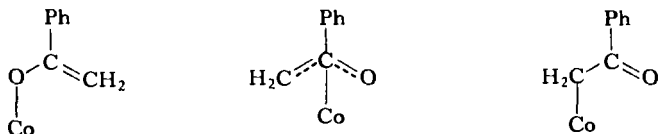
In 1965 Kwiatek and Seyler (109) reported the existence of a cyanide-dependent equilibrium involving σ - and π -allyl complexes, revealed by NMR spectroscopy in aqueous solution, viz.,



If the π -allyl ligand is considered to retain one negative charge, then the cobalt ion remains trivalent. The NMR spectra of fresh solutions of the butenyl analog suggested that it contained the σ -2-butenyl complex, but observation of rearrangement to the π -complex was prevented by decomposition (109). The formation of both σ - and π -complexes explains the remarkable effect of the cyanide concentration on the nature of the products in the homogeneous hydrogenation of butadiene, isoprene, etc. (see Section VII,A). The π -allyl ligand apparently requires two coordination positions, and this type of isomerization is, therefore, far less likely to occur in organocobalt complexes containing a fairly rigid macrocyclic ligand occupying the equatorial coordination positions.

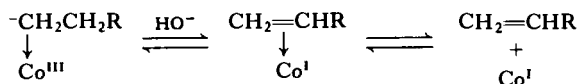
The NMR spectrum of the phenacyl complex $[\text{PhCOCH}_2\text{Co(CN)}_5]^{3-}$ shows only a single resonance due to the methylene group, and it was

suggested (109) that this might be due to a rapid equilibration between different structures such as

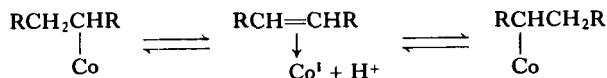


π -Olefin-cobalt(III) complexes have not yet been observed directly, but have been postulated as intermediates in various reactions (see Section VI,B,1,d and the preceding section).

More recently Schrauzer, Weber, and Beckham (159) showed the existence of equilibria involving the loss of a proton from the σ -alkylcobalt(III) complex to give a π -olefin-cobalt(I) complex, i.e.,



The same red π -olefin-Co(I) complex could be formed both by treating the yellow complex $[\text{EtOOCCH}_2\text{CH}_2\text{Co}(\text{DMG})_2\text{py}]$ with base, and by reacting the blue-green Co(I) complex with ethyl acrylate ($\text{CH}_2=\text{CH}_2\text{-COOEt}$) in fairly alkaline solution (0.1–1 *M* NaOH). At lower pH the reaction of the olefin with Co(I) proceeds via the olefin adduct to the σ -alkyl-Co(III) complex (see also Section III,A). The NMR spectra of the analogous complexes with the ligands $\text{NCCH}_2\text{CH}(\text{CN})^-$ and $\text{EtOOC-CH}_2\text{CH}(\text{COOEt})^-$ in pyridine at room temperature showed only a single signal due to the protons of the organo-ligand, ascribed to tautomerization via the π -olefin complex, i.e.,



Other substituted olefins such as acrylonitrile, fumaronitrile, crotononitrile, cinnamonitrile, and diethylfumarate also formed adducts with $\text{Co}^{\text{I}}(\text{DMG})_2$ complexes containing py, H_2O , or PBU_3 and, in one case, with $[\text{Co}^{\text{I}}(\text{DMG-BF}_2)_2\text{py}]$. Second-order rate constants were reported for the formation of several π -olefin-Co(I) complexes from organocobalt(III) complexes containing, for example, $\text{NCCH}_2\text{CH}_2^-$ with DMG, DPG, DMG-BF, py, H_2O , and PBU_3 .

VI

CLEAVAGE OF THE Co—C BOND

Organocobalt(III) complexes as a group may undergo a variety of different thermal and photochemical reactions which lead to cleavage of the Co—C bond. However, individual complexes show surprising differences in their patterns of reaction. The Co—C bond in methylcobalamin, for example, is stable to concentrated sulfuric acid, strong alkali, and cyanide, but is readily broken by Hg(II) ions, while exactly the opposite pattern is observed with 5-deoxyadenosylcobalamin. Both these complexes are extremely light-sensitive in solution in the presence of air, but methylcobalamin is almost insensitive to light in the absence of air.

It is useful to divide their reactions into three broad groups, depending on the regions of the complex and/or the surrounding medium which are involved in the reaction:

(A) Reactions involving only one coordination position (the Co—C bond), where the only role of the surrounding solvent or medium is to facilitate the gain or loss of a proton by the organo-ligand.

(B) Reactions involving one coordination site *and* attack by an external reagent (electrophile, radical, or nucleophile). Since cleavage of the Co—C bond is accompanied by the formation of a new bond between the organo-ligand and the attacking reagent these can be called *transfer reactions*.

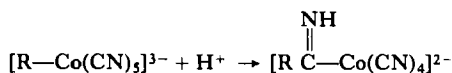
(C) Reactions involving ligands in two adjacent (i.e., *cis*) coordination positions. They include certain *insertion reactions* (e.g., the insertion of cyanide into the Co—C bond) and the reverse *elimination reactions*.

Reactions in both groups A and B may involve homolytic fission of the Co—C bond to give Co(II), or heterolytic fission to give either Co(III) or Co(I) complexes or even (at least in the case of *cis* elimination under A) cobalt hydride complexes [see the general scheme of reactions given in Section I,A]. The course and rates of all these reactions depend not only on the nature of the organo-ligand and the attacking agent (if any), but also on the nature of the other ligands in the complex. Only a few comparisons of rates and products have yet been carried out for complexes which differ only in the second axial ligand or only in the equatorial ligand. These are discussed separately for each type of reaction.

It should be noted that a nucleophilic or electrophilic reagent may bring

about or modify a reaction of the organo-ligand either by direct attack on that ligand or by changing the nature of the axial or equatorial ligands. Substitution of the second axial ligand may occur very rapidly because of the strong kinetic trans effect of the organo-ligand (see Section II,C). A nucleophile (e.g., HO^- or CN^-) may itself substitute the axial ligand, while an electrophile [e.g., H^+ or Hg(II) ions] may protonate or coordinate the axial ligand, thereby causing it to be substituted by a solvent molecule. There are also many cases of the reversible gain or loss of a proton by a macrocyclic ligand. Even the protonation of cyanide (to give Co—CNH) has been shown to be kinetically important in the reactions of the pentacyanides (102) (see also Section VI,D). Such additional reactions and equilibria may complicate the kinetics and their interpretation.

Reactions of group C, which involve interaction between two unidentate ligands in adjacent coordination positions, have so far only been reported for the pentacyanides, most of which undergo reactions to the type:



The presence of a macrocyclic ligand, which preferentially occupies the four equatorial coordination sites, will undoubtedly hinder the occurrence of such reactions in most of the other groups of complexes under discussion. As already mentioned in Section I,A, one of the most important features of the reactions of these complexes is that we can study the reactions of a single organo-ligand uncomplicated (except in the case of the pentacyanides) by reaction with any of the other ligands. However, it should not be overlooked that such macrocyclic ligands do occasionally form octahedral complexes in which they are still tetradentate, but with two adjacent (cis) coordination sites available for coordination by another ligand or ligands [see, for example, refs. (28), (29), (135)]; that trigonal prismatic complexes are also possible; and that a cis position may be made available simply by the reversible dissociation of one donor atom of the macrocycle. Complexes with these configurations might provide mechanistic pathways for insertion or elimination reactions of macrocyclic complexes.

The material is arranged as follows. Photochemical reactions are discussed first (Section VI,A) as they represent the most thoroughly studied and only definitely established examples of the simplest type of reaction, viz., the homolytic fission of the Co—C bond. Thermal (i.e., nonphotochemical)

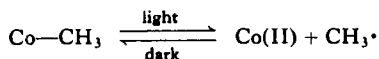
reactions of type A (mainly in solution, but including a few references to the pyrolysis of solids) are discussed in Section VI,B, transfer reactions in Section VI,C, and insertion and elimination reactions (including the insertion of SO_2 , which apparently does not require the prior coordination of SO_2 in the *cis* position) in Section VI,D. Oxidation and reduction are treated briefly in Section VI,E. Equilibria and reactions which involve the organo-ligand but do not lead to cleavage of the Co—C bond have been dealt with in Section V, and catalytic reactions are discussed in Section VII. This section does not aim to be comprehensive. Complete references are given to quantitative mechanistic studies and to transfer (VI,C) and insertion and elimination reactions (VI,D), where the number of papers is small. But some selection has had to be made from among the large number of scattered, often qualitative observations summarized in Sections A, B, and E.

Most of the basic types of reaction were discovered with, or first applied to, the corrinoids (e.g., homolytic cleavage by photolysis, β -elimination to give Co(III) complexes, transfer of the organo-ligand to I_2 , thiols, and nucleophiles such as HO^- and NH_2OH) and with the pentacyanides (e.g., β -elimination to give Co(I) complexes, transfer to Hg(II) as well as I_2 , *cis* elimination of Co—H and, of course, cyanide insertion and decomposition by the cobalt hydride); for dates and references see below. Subsequent mechanistic studies have been carried out mainly with the corrinoids, pentacyanides, and DMG complexes. The most commonly studied ligands are alkyls and substituted alkyls (i.e., with a coordinated tetrahedral carbon atom). There has been relatively little work reported with, for example, alkenyl, aryl, or acyl ligands; this is obviously an area waiting to be explored.

A. Photochemical Reactions

It appears that all organocobalt(III) complexes are light-sensitive. The only complex whose photochemistry has been studied in detail is methylcobalamin. Many other complexes are simply noted as being decomposed by light. We therefore begin by summarizing the experimental results obtained with methylcobalamin and other organocorrinoids. For a fuller discussion and list of references see Chapter 14 of ref. (136). Other complexes are mentioned only where some detailed study has been carried out, or where qualitative observations emphasize significant analogies to or differences from methylcobalamin.

The primary step in the photolysis of methylcobalamin is homolytic fission to give the Co(II) cobalamin and methyl radicals. Recombination can occur, i.e., the reaction is reversed, unless the radicals and/or Co(II) are removed by further reactions:



Photolysis in aqueous solution under nitrogen is very slow and gives Co(II), together with products derived from further reactions of the methyl radical (methane, ethane, ethylene, complexes methylated in the equatorial corrin ligand). The presence of air, however, increases the rate of photolysis by a thousandfold and gives Co(III) together with formaldehyde as the main organic product. The rate can also be increased and the nature of the products changed by the addition of thiols, quinones, and alcohols (in particular isopropanol), all of which react with and remove the methyl radicals.

The photochemically active bands of methylcobalamin have been identified as the intense bands due to $\pi-\pi^*$ transitions within the conjugated corrin ring, and the following quantum yields (ϕ) were obtained: $\lambda = 490$ nm, $\phi = 0.35 \pm 0.04$; 520 nm, 0.32 ± 0.06 ; 550 nm, 0.24 ± 0.05 . Similar quantum yields ($\phi = 0.3-0.5$) were also obtained for the photolysis of methylcobalamin in acid, where the base has been displaced and protonated, and the complex is present as a mixture of the methylquo and five coordinate methyl complexes (140). The effect of varying the second axial ligand on the rate of photolysis by white light has also been studied (134).

Other organo-corrinoids containing higher alkyls, 5-deoxyadenosyl, vinyl, ethinyl, and acetyl have also been shown to produce Co(II) on photolysis under nitrogen, and the accelerating effect of O_2 and of isopropanol demonstrated with other alkyl ligands, in addition to methyl. The rate of photolysis of 5-deoxyadenosyl, however, is unaffected by the presence of oxygen. In this case the radical is rapidly removed, even in the absence of oxygen, by cyclizing onto the adenine. Qualitative comparisons of rates have been made in many cases (usually in the presence of air), but only a few quantitative kinetic studies have been carried out. Most of the complexes with alkyl or substituted alkyl ligands undergo photolysis in air at similar rates. The least light-sensitive organo-corrinoids so far reported appear to be ethinylcobalamin (at least under nitrogen) and carbethoxycobinamide (CoCOOEt).

Among the non-corrinoid complexes, the formation of Co(II) has been established only in the case of organo-salen complexes (37). The accelerating effect of O_2 has been observed in the photolysis of $[MeCo(salen)H_2O]$ (44) and various bis-DMG and bis-DPG complexes (154) and of isopropanol in the photolysis of methyl-bis-DMG complexes (154). Rather surprisingly, the products of the photolysis of many complexes of the type $[RCo(DMG)_2py]$ in chloroform, acetone, or methanol in the presence of air have been shown to be the corresponding peroxide complexes ($ROOCo$) (68, 58). Some of these complexes, where R is a benzyl or allyl ligand, can also form peroxide complexes by a thermal reaction (see Section B,1,a). Close similarities were found in the composition of the gaseous products formed by the photolysis of methyl and ethyl complexes containing corrin, bis-DMG, salen, BAE, and other equatorial ligands under various conditions (different pH, addition of KCN or thiols, etc.) (158). There is obviously a close parallel between these complexes and the corrinoids. Schrauzer and colleagues have compared the rates of photolysis by white light of corrinoid, bis-DMG, and bis-DPG complexes with different organo-ligands and different bases or cyanide in the second axial position, and reported quantum yields in the range 0.0005–0.05 for the photolysis of the complexes with $R = Me$ and Et , $L_4 = (DMG)_2$ and $(DPG)_2$, and $X = H_2O$, NH_3 , py , imidazole, and benzimidazole by light of wavelength ~ 450 nm (154). Kinetic studies have also been reported for certain organo-cobalt-CR complexes (131).

B. Simple Thermal Reactions

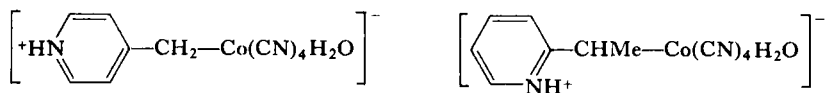
This section deals with reactions which involve only the organo-ligand, whether unmodified or modified by the loss or gain of a proton, and the cobalt. After considering established and possible mechanisms (Section B,1) we list examples to show how reactivity is influenced by different functional groups and substituents (Section B,2), and by changes in the axial and equatorial ligands (Section B,3).

1. Mechanisms

a. *Homolytic Fission.* The primary step in photolysis is homolytic fission to give a Co(II) complex and a free radical; the radical will, of course, usually rapidly undergo further reactions (see Section VI,A). The similarity in the

nature of the products derived from the organo-ligand by photolysis and pyrolysis [see, for example, ref. (158)] suggests that homolytic fission is also the primary step in many pyrolytic reactions. Can homolysis occur in solution at or near room temperature? One would expect this to occur most readily where reasonably stable radicals can be formed. Such may be the case with allyl, benzyl, and related compounds.

Of the complexes $[\text{RCo}(\text{CR})\text{Br}]^+$, those where R is Me or Et are stable at room temperature, the benzyl complex decomposes at a measurable rate, while the allyl complex is too unstable to be isolated. The products of these reactions were not identified (131). Solutions of the complexes $[\text{RCo}(\text{DMG})_2\text{py}]$ react with air at 40°C to give the corresponding peroxide complexes (ROOCo) when R is an allyl or benzyl group, while no reaction is observed even at 80°C when R is a purely aliphatic alkyl group (58). The benzyl pentacyanide is unstable towards air in solution (74), and benzylcobalamin is also reported to be unstable (167). Since O_2 is unlikely to react directly with the undissociated ligand and it is difficult to envisage any other mechanism for the decomposition of the benzyl complexes, it seems reasonable to assume that the benzyl, and probably also the allyl, complexes react via homolytic fission to give $\text{Co}(\text{II})$ and free radicals. It should be mentioned that the complexes $[\text{ArCHMeCo}(\text{DMG})_2\text{py}]$ react with O_2 at room temperature (58) and decompose in both acid and alkaline solution, i.e., decomposition appears to be pH-dependent (163); but here the initial step is probably the elimination of $\text{Co}-\text{H}$ (see Section f). The two anionic complexes shown below contain heteroaromatic analogues of benzyl and it was suggested that the nature of the products of decomposition at pH 0–6 could most easily be explained on the assumption that decomposition occurred via homolysis (100, 102).



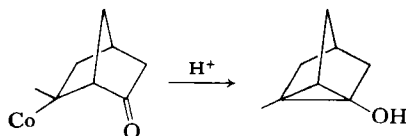
It is possible that the general instability of secondary alkyl ligands such as isopropyl and cyclohexyl (see Section B,2) may also be due to homolytic fission at room temperature, but here also other mechanisms, such as the elimination of $\text{Co}-\text{H}$, are possible.

b. *Unimolecular ($S_{\text{N}}1$, $S_{\text{E}}1$) and Bimolecular ($S_{\text{N}}2$, $S_{\text{E}}2$) Reactions with*

the Solvent. No simple heterolysis to give a carbonium ion (by an S_N1 mechanism) or a carbanion (S_E1) has yet been reported. It seems possible, however, that the formation of the Co—C bond by the reaction of Co(III) complexes with compounds containing an active hydrogen (acetone, nitromethane, malononitrile; see Section III,C) may occur via the intermediate formation of the anion, and that the reverse S_E1 dissociation might be observable under certain conditions.

Most complexes with simple alkyl ligands, especially methyl, appear to be fairly stable towards both acid and alkali. The Co—C bond in methylcobalamin, for example, remains unbroken at room temperature in concentrated H_2SO_4 , water, and 10 *M* KOH [see ref. (136)]. The organo-salen complexes are slowly decomposed by concentrated aqueous acid to give the hydrated Co(II) ion and the products of hydrolysis of the salen ligand (47). It cannot therefore be decided whether acid first attacks the salen or the alkyl group. One possible exception is *trans*-[Me₂Co{(DO)(DOH)pn}], which reacts with acid to give methane (conditions and other products not mentioned) (41). Hydroxide will attack acyl ligands to give carboxylic acids but this probably occurs via the intermediate addition of HO^- to the carbonyl function. This is considered as a transfer reaction (see Section VI,C,2). Certain of the higher alkyls are, however, attacked by alkali, but the products are olefins and Co(I) (159). There is, therefore, no established case of an S_N2 or S_E2 reaction of the simple alkyl ligands with HO^- , H_2O , or H^+ . S_E2 reactions do, however, occur with electrophiles such as Hg(II) (see Section VI,C,1).

c. *Intramolecular Displacement.* Kwiatek (105) has reported a reaction which appears to be a good example of intramolecular displacement. Norbornenone reacts with $[Co(CN)_5H]^{3-}$ to give two products, one of which (presumably the endo form) reacts with acid to give 1-hydroxynortricyclene, i.e.

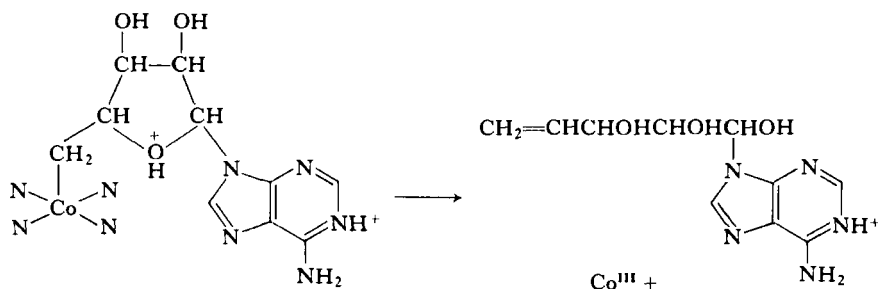


The reaction presumably involves protonation of the oxygen, followed by attack of the carbonium ion ($C^+—OH$) on the coordinated, anionic carbon atom. (The exo form undergoes cyanide insertion in acid; see Section VI,D).

Another reaction which may proceed by intramolecular displacement is the decomposition of $[\text{BrCH}_2\text{CH}_2\text{CH}_2\text{Co}(\text{DMG})_2\text{py}]$ by cyanide to give cyclopropane (162). The pyridine is presumably displaced by cyanide, whose stronger donor power (see Section II,C) places a greater negative charge on the α -carbon atom of the organo-ligand and makes it more susceptible to attack by electrophiles. An intermediate which is probably the $\text{Co}(\text{CH}_2)_3\text{X}$ complex (32) can also be detected in the reaction of $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ with $\text{I}(\text{CH}_2)_3\text{X}$ ($\text{X} = \text{Br}, \text{I}$) to give cyclopropane.

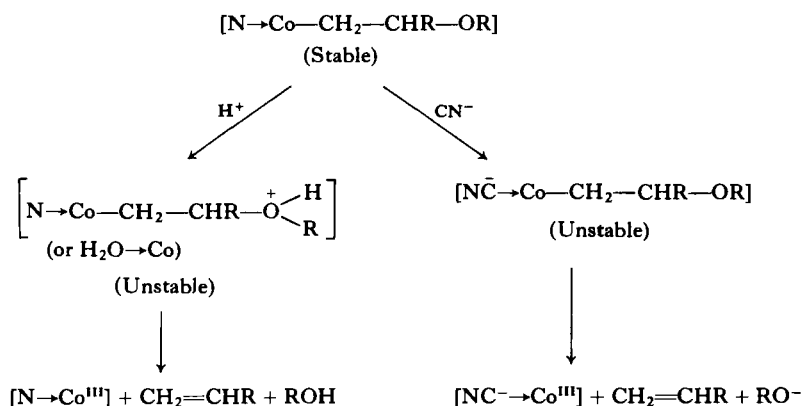
No example of intramolecular displacement to give $\text{Co}(\text{I})$ has yet been reported. β -Hydroxyethyl complexes are decomposed by alkali to give $\text{Co}(\text{I})$ and acetaldehyde, and it has been suggested (33) that this might proceed via the intermediate formation of the epoxide. But the results are more easily explained on the basis of the established mechanism involving the cis elimination of $\text{Co}-\text{H}$ (see Section f).

d. *Elimination to give Co(III)*. The first reactions of this type to be discovered and elucidated relate to the 5-deoxyadenosylcorrinoids, which are stable in neutral and alkaline solution, but are decomposed by heating in dilute acid and by the action of cyanide. Both these reactions were discovered by Barker and co-workers in 1958 in the course of isolating the compounds, i.e., before their structures were known. Decomposition in acid is probably initiated by protonation of the ring oxygen of the sugar, followed by elimination of $\text{Co}(\text{III})$ and oxygen (as ROH) from the α and β -carbon atoms, respectively, i.e.,



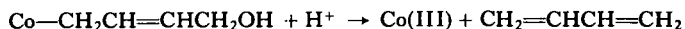
Decomposition by cyanide gives the same products (except that the sugar forms the cyanhydrin) and probably involves coordination of cyanide in the trans position, followed by the elimination of $\text{Co}(\text{III})$ and oxygen (as RO^-) to give the olefin. For further references and discussion about both these reactions see Chapter 13 of ref. (136). These two methods of decomposition

can be written schematically as follows (the heterocyclic base is denoted by N):



This shows that the activation energy for elimination can be reduced by either increasing the electron density on the α -carbon (by ligands of greater donor strength) or decreasing the electron density on the β -carbon.

In 1965 Hogenkamp, Rush, and Swenson reported rate constants for the decomposition to ethylene of cobalamins containing the simpler ligands $\text{HOCH}_2\text{CH}_2-$ and $\text{MeOCH}_2\text{CH}_2-$ in dilute acid at 100°C , and suggested that the reaction involved protonation of the oxygen atom, followed by a concerted elimination of Co(III) and H_2O or MeOH (89). The same mechanism has also been suggested for the reactions of the analogous pentacyanides (105). A 1,4-elimination has also been reported for a pentacyanide (105), viz.,



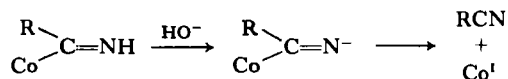
In 1965 Kwiatek and Seyler (110) reported that the pentacyanides containing allyl or phenacyl ligands react with acid to give the corresponding olefins and ketones. (Most organopentacyanides undergo cyanide insertion reactions in acid; see Section VI,D.) They proposed a mechanism involving initial protonation to form a complex with a positive charge on the β -carbon, which can then lose Co(III) either directly or via the intermediate formation of a π -olefin or π -enol complex.

In none of the reactions discussed above is there any direct evidence as to whether elimination is *cis* or *trans*, concerted or stepwise, and, if stepwise, via the intermediate formation of a Co(III) π -complex. The very rapid

hydrolysis and alcoholysis of the complexes $[\text{CH}_3\text{COOCHRCH}_2\text{Co}(\text{DMG})_2\text{py}]$ does, however, suggest the intermediate formation of some complex which could be written as either a carbonium ion ($\text{CoCH}_2\text{CHR}^+$) or, more likely, as the π -olefin complex (69) (see also Section V,B).

No β -bromo- or iodoalkyl complexes have yet been isolated. The reaction of vicinal dibromides or diiodides with $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$, $[\text{Co}(\text{CN})_5\text{H}]^{3-}$, or a $\text{Co}(\text{I})$ -DMG complex merely gives the olefin (32, 75, 105, 109, 161), though kinetic evidence was obtained for the intermediate formation of the β -bromo complex in the reaction of $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ with α,β -dibromopropionate and α,β -dibromosuccinate (75). It is interesting that the pentacyanide produced is the bromo or iodo, and not the aquo, complex (32, 75), which suggests that the decomposition may involve a cis rather than a trans elimination of $\text{Co}-\text{X}$. The β -chloroethyl complex can be prepared by the reaction of $[\text{Co}(\text{CN})_5\text{H}]^{3-}$ with $\text{ClCH}_2\text{CH}_2\text{I}$ (105).

e. *Elimination to Give Co(I)*. The first mechanism of this type was proposed by Kwiatak and Seyler (110) for the second step in the formation of nitriles from the organopentacyanides, but the individual steps in the reaction were established by Johnson, Tobe, and Wong (101, 102). The complexes $[\text{RC}(=\text{NH})\text{Co}(\text{CN})_4]^-$, which are formed from $[\text{RCo}(\text{CN})_5]^{3-}$ in acid, react in alkaline solution to yield nitriles. Johnson *et al.* suggested a mechanism involving the loss of a proton from the nitrogen, followed by elimination of $\text{Co}(\text{I})$, i.e.,



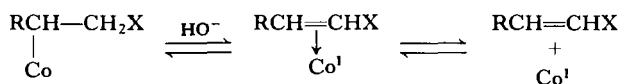
It is, of course, possible that there may be an intermediate in which the nitrile is π -bonded to the metal.

A second reaction of this type, discovered by Barnett, Hogenkamp, and Abeles in 1966 (7), is the decomposition of β -cyanoethylcobalamin by alkali according to the equation



The rate showed a first-order dependence on the concentrations of both hydroxide and the cobalt complex, and Hogenkamp (89) suggested that the initial step was the removal of a proton from the β -carbon, followed by the elimination of $\text{Co}(\text{I})$. Schrauzer, Weber, and Beckham (159) were subsequently able to show the formation of π -olefin- $\text{Co}(\text{I})$ complexes in

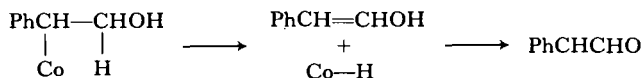
the reversible formation and decomposition of complexes of the type $[XCH_2CHRCo(DMG)_2py]$, where X is CN or COOEt, and they reported rate constants for some of these reactions (see also Sections III,A and V,C). We can, therefore write the general reaction



But it should be emphasized that there is no proof that the π -olefin complex is an essential intermediate in any or all of these reactions.

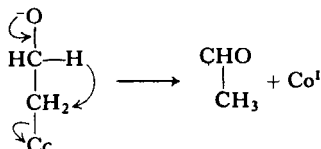
f. *Cis Elimination of Co—H*. In 1968 Jackman, Hamilton, and Lawlor (94) showed that the formation of adducts from $[Co(CN)_5H]^{3-}$ and α,β -unsaturated acids involved the stereospecific *cis* addition of Co—H to the olefinic bond (see also Section III,A), and Johnson, Tobe, and Wong (102) showed that the reaction of the hydride with α -vinylpyridine to give the α -(2-pyridioethyl)cobalt complex was reversible, though no direct evidence as to the mechanism was obtained. However, it seems reasonable to assume that the same *cis* addition or elimination operates in both cases.

The *cis* elimination of Co—H was conclusively established by Gaudemer and co-workers (129) for the decomposition of $[HOCH_2CHPhCo(DMG)_2py]$ in methanol at 40°C, which gives $PhCH_2CHO$ and the Co(I) or cobalt hydride complex as the final products. They used the rapid *cis* addition of CoH to phenylacetylene (see Section III,A) to detect the intermediate formation of CoH and the origin of the hydrogen. The decomposition of the deuterated $CoCHPhCD_2OH$ in CH_3OH in the presence of $PhC\equiv CH$ gave $CoCHPh=CHD$ (and $PhCH_2CHO$), i.e., the deuterium of Co—D originated from the β -carbon of the original ligand, and decomposition of the undeuterated complex in CH_3OD gave mainly $PhCHDCHO$, i.e., the formation of the aldehyde involved the uptake of a proton from the solvent and not an intramolecular hydride shift. They proposed a *cis* elimination of CoH, followed by isomerization of the enol to the aldehyde, i.e.,

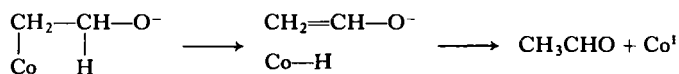


β -Hydroxyethyl complexes, whether corrinoids (155), bis-DMG (162), or porphyrins (33), are all decomposed by alkali at room temperature to give Co(I) and acetaldehyde, and there has been considerable interest in

the possible mechanisms because of the fact that some of the corrinoid-catalyzed enzymatic reactions involve the isomerization of glycols to aldehydes (see Section VII,D). Johnson and co-workers (33) have suggested the intermediate formation of the epoxide, while Schrauzer [see, for example, ref. (155)] favors a 1,2-hydride shift, i.e.,



but no experiments using deuterated ligand have yet been carried out. One could, however, equally well envisage a mechanism analogous to that established by Gaudemer, involving the cis elimination of CoH from the alkoxide, followed by isomerization of the vinyl alcohol, i.e.,



This mechanism requires that the cis elimination of CoH occurs more readily with the alkoxide than the alcohol form of the ligand. Although this is possible, since alkoxides are better hydride donors than alcohols, Gaudemer and colleagues did not study the pH dependence of their reaction, and there is therefore no direct experimental evidence on this point. Alkaline cleavage to give an aldehyde or ketone is also observed for DMG complexes with ligands such as $-\text{CH}_2\text{CHMeOH} (\rightarrow \text{CH}_3\text{COCH}_3)$, $-\text{CHMeCH}_2\text{OH} (\rightarrow \text{CH}_3\text{CH}_2\text{CHO})$, $-\text{CH}_2\text{CHOHCH}_2\text{OH} (\rightarrow \text{CH}_3\text{COCH}_2\text{OH})$, but not $-\text{CH}_2\text{CMe}_2\text{OH}$ (162, 155), and rate constants have been reported for several β -hydroxyalkyl complexes of this type (155).

2. The Effect of Substituents and Functional Groups

Tables IV and V list examples to show the effect of functional groups and substituents on the course and rate of reactions involving cleavage of the Co—C bond in acid, neutral, and alkaline solution in the absence of any other added reagent. Transfer reactions involving HO^- (see Section VI,C,2), cyanide insertion (VI,D,1), and irreversible reactions not involving cleavage of the Co—C bond (V,B) are also included in order to complete

TABLE IV

REACTIONS SHOWN BY ORGANO-LIGANDS WITH DIFFERENT FUNCTIONAL GROUPS

Abbreviations

Complexes: corrin Corrinoids

DMG Bis-DMG complexes

pc Pentacyanides

(other abbreviations as given in Section I,B)

Solution: H acid

N neutral

HO alkaline

} approximate and qualitative, since the pH is usually not stated

Reactions/products: CN Cyanide insertion (see Section VI,D)

hom. Probably homolytic fission (see Section B,1,a)

isom. Isomerization of β - to α -substituted ethyl complex (see text)

Other products stated, where reported

+ Reaction observed, but products not reported

— No reaction observed

1. Groups attached directly to the cobalt (Co—X)

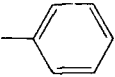
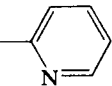
X	Complexes	Solution	Reactions/products	References
—CH ₃	All very stable to H and HO except: pc H (Me ₂ Co{(DO)(DOH)pn})	H CN		110
—CH ₂ R	corrin DMG pc	H H HO H N	CH ₄ — — Co ^I , olefins CN +	41 136 62, 136 159 105, 110 74
—CHR ₂	corrin DMG pc	N N N	+ ? + +	61 163 105
—CR ₃	Not known			
—CH=CHR(H)	corrin	H HO	+ —	77 62, 136
—CH=CH—Co	pc pc	H ? N N	CN CN +	110 105 70
—CH=C=CH ₂	DMG	H	Co—CH ₂ COCH ₃	99
—C≡CH	corrin	H	Co—COCH ₃	77
	pc	H	CN	110

TABLE IV *continued*

1. Groups attached directly to the cobalt (Co—X)

X	Complexes	Solution	Reactions/products	References
	pc	H	—	75
NH -CR	tetracyanide	H	Co—COR	101, 102
-COR	corrin	HO	Co ¹ , RCN	101, 102, 110
-COOR	salen and 7-Me-salen	H	—	15, 77
		HO	Co ¹ , RCOOH	15, 180
-COCl	corrin	H	Co ³ , CO, ROH	45
		HO	—	45
		N	+	126

2. Substituted methyl ligands (Co—CH₂X)

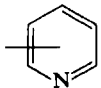

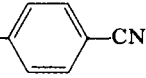

X	Complexes	Solution	Reactions/products	References
-H, R	See under (1)			
-CH=CHR	DMG	H	CH ₂ =CHCH ₂ R (R = H, Me)	162
		N	hom. (R = H, Me)	58
	pc	H	CH ₂ =CHCH ₂ R (R = H, Me)	109, 110
		N	propene (R = H); butadiene and butenes (R = Me)	109
		HO	-(R = H); butadiene and butenes (R = Me)	109
	CR	N	+(R = H)	131
	pc	H	CN, hom.	100, 101
		N, HO	—	100, 101
(2,3,4-isomers)				
-CN	pc	H	—	105
-CHO	DMG	HO	—	162
-COR	pc	H	CH ₃ COR	110
-COOH	corrin	H, HO	—	91a
-COOR	corrin	H	—	91a
	DMG	H, HO	—	163

TABLE IV *continued*3. Substituted ethyl ligands (Co—CH₂CH₂X)

X	Complexes	Solution	Reactions/products	References
-H, R	See under (1)			
-CN	corrin	H	—	89, 91a
		HO	Co ^I , CH ₂ =CHCN	7, 89, 159
	DMG	HO	Co ^I , CH ₂ =CHCN; also isom.	159, 163
	(DPG) ₂	HO	Co ^I , CH ₂ =CHCN	159
	(DMG—BF ₂) ₂	HO	Co ^I , CH ₂ =CHCN	159
	porph	HO	—	155
-COOH	corrin	H, HO	—	89, 91a
	DMG	HO	—	159
-COOR	corrin	H	—	89, 91a
		HO	Co ^I , CH ₂ =CHCOOR	89, 159
	DMG	H	CoCH ₂ CH ₂ COOH	163
		HO	Co ^I , CH ₂ =CHCOOR; also isom.	159, 163
-Cl	pc	N	Apparently —	105
-Br	DMG, pc	N	Co ³ , olefin (See section B,1,d)	
-F, I	Not known			
-OH	corrin	H	Co ³ , ethylene	89
		HO	—	89
			Co ^I , CH ₃ CHO	155
	DMG	H	ethylene	162
		HO	Co ^I , CH ₃ CHO	162
	pc	H	ethylene	105
		? HO	Co—H, CH ₃ COR	103
	porph	HO	CH ₃ CHO	33
			—	155
	(DMG—BF ₂) ₂	HO	CH ₃ CHO	155
	salen	HO	CH ₃ CHO	155
	(DO)(DOH)pn	HO	CH ₃ CHO	155
-OR	corrin	H	Co ³ , ethylene	89
		HO	—	89
	DMG	H	ethylene	162
		HO	—	162
	pc	H	ethylene	105
-OCOR	DMG	N	+ (Some Co—C cleavage in addition to rapid solvolysis)	69
-NH ₂	corrin	H, HO	—	89
-NR ₃ ⁺	corrin	H, HO	—	89

TABLE V

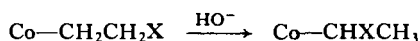
QUALITATIVE COMPARISON OF THE STABILITY OF PENTACYANIDES $[\text{RCo}(\text{CN})_5]^{3-}$ CONTAINING PRIMARY, SECONDARY, AND TERTIARY ALKYL LIGANDS^a

Ligand (R = H or CH ₃)	Primary (-CH ₂ X)	Secondary (-CHMeX)	Tertiary (-CMe ₂ X)	References
$-\text{CR}_2$ - 	++ ^b	—	—	108
$-\text{CR}_2$ - 		+		108
$-\text{CR}_2\text{R}'$	++	+	—	108
$-\text{CR}_2-\text{CH}=\text{CH}_2$	++	+	—	108
$-\text{CR}_2$ - 	++	+		108, 101, 102
$-\text{CR}_2\text{COR}'$	++	++	—	108
$-\text{CR}_2\text{COOH}$	++	++	—	75, 94
$-\text{CR}_2\text{COOR}'$	++	++	+	108
$-\text{CR}_2\text{CN}$	++	++	++	108

^a ++, Stable complex known; +, unstable complex known; —, no complex known.

^b But see Table IV and Section B,1,a.

the picture; but reversible changes such as the formation of π -allyl-Co(III)-tetracyanides and π -olefin-Co(I) complexes (see Section V,C) are excluded. The isomerization reactions mentioned in Table IV are reactions of the type



where X is CN or COOR (163, 159). These reactions probably occur via the elimination of Co(I) and H⁺ to give the olefin (see Section B,1,e), which then adds CoH to give the isomer (see III,A).

The Tables are not comprehensive. Many other complexes have, of course, been prepared with these and other simple organo-ligands, but their reactions in solution have not been reported; and even where mention is made of complexes in neutral solution, we include only those which are reported to be unstable and exclude the numerous cases where no reaction

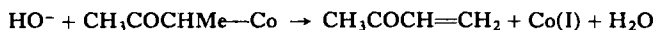
is observed. More complicated organo-ligands have been omitted from the tables, although a few (e.g., 5-deoxyadenosyl) provide good examples of particular reaction mechanisms and have been discussed in the previous section. The terms "acid" and "alkaline" are qualitative, since the pH and other experimental conditions are often not quoted. Differences in pH may explain discrepancies between the observations of different workers. Organo-cobalt-salen and BAE complexes are stated to dissolve in dilute acid without decomposition, but no individual complexes are specifically mentioned (49, 47).

Most of the examples listed are pentacyanide, corrinoid, or DMG complexes. The axial ligands are not identified in the tables, but are as follows: corrinoids, 5,6-dimethylbenziminazole (cobalamins), H_2O or none (cobinamides), $(\text{DMG})_2$, usually pyridine or H_2O , less frequently NH_3 , imidazole, benzimidazole, PBU_3 , etc. The nature of the axial and equatorial ligands may have a striking effect on reactivity, but few direct comparisons are available; these are discussed in the next section.

Table IV summarizes the effect of different functional groups attached to the cobalt and to the α - and β -carbon atoms, while Table V shows more qualitatively the effect on the stability of the organopentacyanides of changing the functional group and/or the number of methyl groups attached to the α -carbon. The data in Table IV show that if we neglect the cyanide insertion reactions, there are remarkable similarities between the pentacyanides, corrinoids, and DMG complexes. There are even indications that the pattern of reactivity exhibited by the pentacyanides and shown in Table V may also apply to the other complexes. For example, DMG complexes with tertiary butyl (147) or the secondary alkyl ligands ArCHMeCo are unstable (163, 129, 58), perhaps also the isopropyl complex (163, 147), while the complex with the tertiary ligand $-\text{CMe}_2\text{CN}$ can readily be prepared in good yield (163). Isopropyl-, cyclohexyl-, and *tert*-butyl-corrinoids are also unstable (61, 19, 147, 154). One would expect most other organocobalt(III) complexes to show the same general pattern of reactivity.

The data of Tables IV and V show that the nature and position of the substituents exert a subtle control over the course and rate of reaction; compare, for example, $-\text{CH}_2\text{CH}_2\text{OH}$ with $-\text{CH}_2\text{CH}_2\text{OR}$ or $-\text{CH}_2\text{CH}_2\text{NH}_2$. One of the most obvious features to emerge is that heterolysis to give Co(III) occurs in acid, and heterolysis to give Co(I) in alkaline solution, though there may be some exceptions to this general rule. For example, it has been

reported (163) that the alkaline cleavage of the α -acetylethyl-bis-DMG complexes gives mainly $\text{CH}_3\text{COCH}_2\text{CH}_3$ and Co(III) , with only small amounts of the products expected according to the reaction



One would expect that homolytic fission, and perhaps even the elimination of CoH , would occur in both acid and alkaline solution, but there is little information on this point.

Table V indicates which organopentacyanides can and cannot be prepared and which are unstable. The inability to observe any given complex may, of course, be due to the nonformation of that complex rather than to its rapid decomposition; but, in view of the isolation of several unstable complexes, it seems reasonable to accept the inability to isolate a complex as circumstantial evidence for its instability. Examination of the data in Table V shows that instability may be enhanced by increasing either (1) the electropositive character or +I inductive effect of the substituent (which is greatest at the top of the column of ligands in the table), or (2) the number of methyl (and presumably other) groups on the α -carbon. The destabilizing effect of replacing hydrogen by methyl can obviously be ascribed both to a greater inductive effect and to increased steric compression. It also opens up additional pathways such as the elimination of CoH (Section B,1,f). There is, unfortunately, little positive evidence as to the mechanisms involved in the decomposition of the secondary and tertiary ligands except that the α -(2-pyridyl)ethyl complex undergoes elimination of CoH (see Section B,1,f). Pentacyanides and other complexes with simple secondary alkyl ligands might decompose by homolytic fission, as in benzyl and allyl complexes (see Section B,1,a), or by the elimination of Co(I) to give an olefin, as apparently occurs with higher primary alkyls (see Table IV). The fact that cyclohexylcobalamin is stable in acid, but unstable in neutral and alkaline solution, and gives cyclohexene as the main organic product (154) supports the latter mechanism in this particular case. The PhCHMeCo(DMG)_2 complexes, on the other hand, are readily cleaved in mildly acid and alkaline solution (163). This suggests the occurrence of a pH-independent mechanism such as homolysis (as in the benzyl complexes) or elimination of CoH .

A few complexes are known with substituents in the γ - or δ -positions, which allow one to see the effect of chain length. Of the DMG complexes

with the ligands $\text{Co}(\text{CH}_2)_n\text{Br}$, the β -bromoethyl is probably formed as an unstable intermediate (see Section B,1,d), the γ -bromopropyl will form cyclopropane on heating or on treating in solution with cyanide (see Section B,1,c), while the δ -bromobutyl is apparently stable (162). No complexes of the type CoCH_2Br are known. This shows the expected decrease in influence of the substituent as it moves away from the cobalt. Of the DMG complexes with the ligands $\text{Co}(\text{CH}_2)_n\text{OH}$, only the complex with $n = 2$ is unstable to acid, while those with $n = 3$ and 4 are both stable (162).

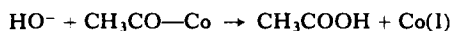
3. Effect of the Axial and Equatorial Ligands

There are many qualitative observations, but few direct quantitative comparisons, which demonstrate the effect of changing the axial (X) or equatorial (L_4) ligands. The main problem is that no quantitative studies have yet been made of the rates and equilibria of ligand substitution involving the axial ligand (X) in relevant organo-Co-DMG complexes and only a few involving the organocorrinoids.

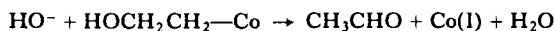
The decomposition of 5-deoxyadenosylcorrinoids [in which X is a heterocyclic base, H_2O , or absent; see ref. (136)] to give Co(III) and an unsaturated sugar has already been discussed in Section B,1,d. These complexes are stable in neutral solution, but elimination occurs under the influence of either acid, which protonates the $\text{CoCH}_2\text{CHROR}'$ group, or cyanide, which becomes the axial ligand in the transient intermediate. The compound $[\text{5-deoxyadenosyl-Co(DMG)}_2\text{py}]$ is also decomposed by either acid or cyanide to give the unsaturated sugar (183, 155). β -Hydroxyethyl complexes will liberate ethylene to give Co(III) in acid (see Table IV). In the case of the DMG complexes, at least, this occurs far more readily when $\text{X} = \text{CN}^-$ (or, apparently, unspecified mercaptans or thiolate anions RS^-) than when $\text{X} = \text{H}_2\text{O}$, py, or PBu_3 (162). Another example, which has already been mentioned in Section B,1,c, is $[\text{Br}(\text{CH}_2)_3\text{Co(DMG)}_2\text{py}]$, which liberates cyclopropane [and presumably Co(III)] on treating with cyanide (162). There are, therefore, several examples of reactions leading to the formation of Co(III), in which CN^- exerts a strong labilizing effect. Cyanide and 5,6-dimethylbenzimidazole (Bzm) both exert a stronger labilizing effect than H_2O (or no ligand) in the transfer of carbanions to Hg(II) and Tl(III) ions (see Section C,1). One would expect that reactions leading to the loss of a carbanion and/or the formation of Co(III) would be accelerated by ligands of greater donor strength. Since numerous studies on the ground-state, thermodynamic, and kinetic properties of Co(III)

complexes have shown that the unidentate ligands can be placed in an order related to their donor power, and in particular that donor power falls in the order $\text{CN}^- > \text{Bzm}$, py , $\text{NH}_3 > \text{H}_2\text{O}$ (139, 78), the limited data available show that the effect of the axial ligand on the rate of heterolysis of the $\text{Co}-\text{C}$ bond to give Co(III) parallels its effect on other ground-state, thermodynamic, and kinetic properties of the complexes. The cobalamin $\text{CoCH}_2\text{CH}_2\text{NMe}_3^+$ (89) and the cobinamide CoCOOEt (184) are two other complexes which are decomposed by cyanide and presumably give Co(III) , the former with ethylene and NMe_3 , the latter with CO and EtOH .

A different order of ligands is found for reactions leading to the formation of Co(I) . In the transfer reaction (see also Section C,2)



the cobinamide ($\text{X} = \text{H}_2\text{O}$ or absent) reacts about six times faster than the cobalamin ($\text{X} = \text{Bzm}$) (67). Cyanide appears to have no effect on the rate (180). The decomposition of β -hydroxyethylcorrinoids according to the reaction



is also faster for the cobinamide than the cobalamin ($K_2 = 9.9 \times 10^{-4}$ and $1.5 \times 10^{-4} \text{ M}^{-1} \text{ sec}^{-1}$, respectively, at 27°C) (155). It is not known whether these cobinamides are five- or six-coordinate or mixtures; but the data suffice to establish the order of labilizing power of the axial ligands: H_2O or none $> \text{Bzm}$ and possibly CN^- . The order for heterolysis to give Co(I) is, therefore, the reverse of the order for heterolysis to give Co(III) . Rate constants have also been reported for the reactions of hydroxide with solutions of the complexes $[\text{HOCH}_2\text{CH}_2\text{Co(DMG)}_2\text{X}]$, where X is H_2O , benzimidazole or pyridine, to give Co(I) and CH_3CHO (155), and of the complexes $[\text{NCCH}_2\text{CH}_2\text{Co(DMG)}_2\text{X}]$, where X is H_2O , pyridine, or PBu_3 , to give the π -olefin- Co(I) complex (159), but the identity of the axial ligands under the experimental conditions was unfortunately not established.

The decomposition of 4-pyridylmethyl- and α -(2-pyridyl)ethylpenta-cyanide, which probably involves homolytic fission (see Section B,1,a), occurs only after the loss of one cyanide to give the (presumably trans) organotetracyanoaquo complexes (100, 102), i.e., in this case we observe the order $\text{H}_2\text{O} > \text{CN}^-$. The decomposition of corrinoids possessing secondary alkyl ligands is accelerated by the addition or presence of bases and cyanide. Isopropylcobalamin is more unstable than the cobinamide (61); cyclohexyl-

cobinamide is decomposed by the addition of cyanide (19) and cyclohexylcobalamin by the addition of imidazole or cyanide (154). Both the cobalamins and cobinamides are five-coordinate (136), so that we have here the order: CN^- , imidazole, Bzm > none. For possible mechanisms of reaction see the previous section. Cyanide will also slowly decompose methyl- and ethylcobalamin, but the reaction requires oxygen and the mechanism is unknown [see the discussion in Chapter 13 of ref. (136)].

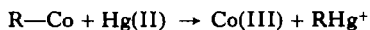
In view of these examples of the pronounced effect of the nature of the axial ligand (X), comparisons of the effects of different equatorial ligands are obviously meaningful only when it is shown conclusively that X remains constant. Kinetic studies have been carried out with organocobalt(III) complexes possessing different equatorial ligands for reactions of ligands such as β -cyanoethyl with hydroxide (159), β -hydroxyethyl with hydroxide (155), and 5-deoxyadenosyl with acid, hydroxide, and cyanide (155). However, with none of these reactions has it been established that X remains constant for the complexes being compared.

C. Transfer Reactions

Transfer reactions are here defined as reactions in which a new bond is formed between the leaving organo-ligand (usually at the α -carbon) and the attacking reagent (but excluding a proton). The reaction of $[\text{Me}_2\text{-Co}\{(\text{DO})(\text{DOH})\text{pn}\}]$ with acid to give methane (41) has already been mentioned (Section B,1,b). Transfer may occur to electrophiles, nucleophiles, metal ions, and possibly radicals. We consider first reactions of known or likely mechanisms involving transfer to electrophiles (Section C,1) and nucleophiles (C,2), then other reactions of unknown mechanism (C,3).

1. Transfer to Electrophiles

a. *Hg(II) Ions.* Many organocobalt(III) complexes react with Hg(II) ions



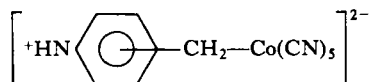
The first reaction of this type, the reaction of HgCl_2 with $[\text{CH}_3\text{Co}(\text{CN})_5]^{3-}$ to give CH_3HgCl was reported in 1964 (74). Since then work on the pentacyanides, the corrinoids, and DMG complexes has provided an insight into several features of the reaction.

Adin and Espenson (1) have studied the kinetics and products of the reactions of $[\text{RCo}(\text{DMG})_2\text{H}_2\text{O}]$ with $\text{Hg}(\text{II})$ ions in aqueous HClO_4 . The reactions are first order with respect to both mercury and the cobalt complex. Since the rate is drastically reduced by addition of chloride ions [i.e., $\text{Hg}(\text{II})$ is more reactive than HgCl^+ , etc.], they concluded that the reaction proceeded by an $\text{S}_{\text{E}}2$ rather than an $\text{S}_{\text{E}}1$ mechanism. And since the rate is also reduced by substitution at the α -carbon ($\text{Me} > \text{Et} > i\text{-Pr}$) but not at the β -carbon ($\text{Et} \sim n\text{-Pr} \sim i\text{-Bu}$), they concluded that the $\text{Hg}(\text{II})$ ion attacks the coordinated carbon atom from the same side as the cobalt ion. One could envisage an intermediate in which the mercury is coordinated to one of the donor nitrogen atoms of the equatorial ligand. The lower rate of the ethyl compared to the methyl complex is associated with a much higher activation energy ($\Delta H = 20.5$ and 16.2 kcal/mole, respectively). A kinetic cis effect was also observed. The equatorial $(\text{DMG})_2$ ligand, which contains two $=\text{N}-\text{OH}$ and two $=\text{N}-\text{O}^-$ groups and in which the two halves are held together by hydrogen bonds ($=\text{N}-\text{O}^- \cdots \text{H}-\text{O}-\text{N}=\text{O}$), can reversibly pick up an additional proton to give a structure which probably contains three $=\text{N}-\text{OH}$ groups and one $=\text{N}-\text{O}^-$ and hence only one hydrogen bond. In agreement with their greater electron-withdrawing power (which would destabilize the transition state, involving removal of the organoligand as the carbanion), these protonated complexes react at a far lower rate. The complex $[\text{CH}_3\text{Co}(\text{DMG}-\text{BF}_2)_2\text{H}_2\text{O}]$ also reacted more slowly than $[\text{CH}_3\text{Co}(\text{DMG})_2\text{H}_2\text{O}]$, by a factor of at least 2×10^5 . This was ascribed to a combination of steric hindrance and greater electron-withdrawing power of the equatorial ligand (1). Rate constants have also been reported for the dealkylation of $[\text{RCo}(\text{DMG})_2\text{py}]$ by mercury(II) acetate (160). The rates varied with R in the order $\text{Me} > \text{Et}$ and other primary alkyls $>$ secondary alkyls. Unfortunately, direct comparison with the above data for the aquo complexes, which would provide evidence for the relative trans-labilizing effect of H_2O and pyridine, is not possible because of differences in ionic strength and in the nature of the $\text{Hg}(\text{II})$ species.

The organo-corrinoids show similar behavior, but also additional complications. Rate constants have been determined (84) for the attack of mercury(II) acetate on various organocobalt cobinamides ($\text{X} = \text{H}_2\text{O}$ or absent) and cobalamins ($\text{X} = 5,6\text{-dimethylbenzimidazole}$). The first complication, which has to be born in mind when comparing the cobinamides with the cobalamins or DMG complexes, is that the organocobinamides are partly ($\text{R} = \text{vinyl}$ and methyl) or wholly ($\text{R} = \text{Et}$, $n\text{-Pr}$, $i\text{-Pr}$,

5-deoxyadenosyl) five-coordinate, while the organocobalamins are almost entirely six-coordinate. Secondly, analysis of the kinetics of attack on the organocobalamins is complicated by the fact that Hg(II) ions may complex with the heterocyclic base and displace it from coordination to the cobalt, thereby converting the cobalamin essentially into a cobinamide. As in the case of the DMG complexes, the addition of chloride ions lowers the rate (138). Comparison of the rate constants (84) shows, first, that the rate varies with the degree of substitution on the α -carbon in the order $\text{Me} \gg \text{Et} < i\text{-Pr}$. The greater rate of $i\text{-Pr}$ compared to Et, which is not observed in the DMG complexes, was ascribed to a weakening of the Co—C bond by steric compression within the secondary alkyl ligand and between it and the corrin ring and to associated electronic changes. There may, of course, also be a change in mechanism. Second, the heterocyclic base 5,6-dimethylbenzimidazole exerts a trans-labilizing effect compared to H_2O (or, in the case of the five-coordinate cobinamides, no ligand) in all three cases where data are available ($\text{R} = \text{vinyl}, \text{Me}, \text{Et}$). Since the heterocyclic base is a better donor than H_2O , this is the expected order of ligands for a reaction involving the removal of a carbanion. For some other data on organo-corrinoids see ref. (160).

Finally, Bartlett and Johnson have investigated the reactions of the 2-, 3-, and 4-pyridiomethylpentacyanide complexes



with Hg(II) and Tl(III) chloride complexes (8). Their rate constants show that reactivity decreases as the number of chloride ligands on the Hg(II) ion increases. In the absence of added chloride, however, HgCl_2 removes CN^- to give $\text{Hg}(\text{CN})_2$ and the complex $[\text{RCo}(\text{CN})_4\text{H}_2\text{O}]$, which is not attacked by Hg(II) ions. This shows the labilizing effect of CN^- compared to H_2O , again in agreement with the expected order.

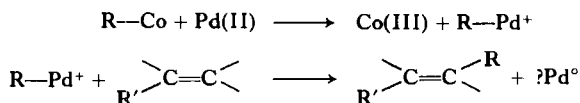
The above results show that the reactions of all organocobalt(III) complexes with Hg(II) ions so far reported share several features in common. The reaction proceeds by an $\text{S}_{\text{E}}2$ mechanism and the rate is reduced [compared to that of the simple aquated Hg(II) ion with the methyl complex] by (1) complexing of the Hg(II), e.g., with chloride, (2) increased substitution on the α -carbon, and (3) reduced electron donation from the cis and/or trans ligands.

The *in vivo* formation of toxic methylmercury compounds probably involves methylation by methylcorrinoids [see Section VII,D and Chapter 17 of ref. (136)].

b. *Tl(III)*, *Ag(I)*, *Co(III)*, and *Pd(II)*. Several other metal cations have been tested for transalkylation reactions. As already mentioned, *Tl(III)* chloride complexes react with all three pyridiomethylpentacyanide complexes to give the corresponding organothallium compounds. Reactivity falls in the order $\text{TlCl}_2^+ > \text{TlCl}_3 > \text{TlCl}_4^-$ and the rates are, in general, greater than those of *Hg(II)*. Indium(III) chloride reacts rapidly and gallium(III) chloride slowly with the 4-pyridiomethyl complex, but the reaction probably involves merely abstraction of a cyanide ligand. No reactions were observed with AgNO_3 or H_2PtCl_6 (8). Methylcobalamin also reacts with *Tl(III)* ions, but no organothallium compound was isolated. In the presence of chloride the sole product was methyl chloride. No reactions occurred with *Tl(I)*, *In(III)*, *Cd(II)*, or *Pb(II)* ions (2).

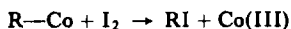
Silver ions do not dealkylate organo-corrinoids at any significant rate, though they reversibly coordinate to the $\text{CoC}\equiv\text{CH}$ and $\text{CoCH}=\text{CH}_2$ groups (84). Silver ions do, however, react with $[\text{Me}_2\text{Co}\{(\text{DO})(\text{DOH})\text{pn}\}]$ to give metallic silver and ethane, presumably via the intermediate formation of the unstable AgCH_3 . The same complex will also react in methanol or aqueous THF at room temperature with the diaquo-*Co(III)* complexes of BAE, salen, saloph, and $\{(\text{DO})(\text{DOH})\text{pn}\}$ and with aquocobalamin to give the methyl derivatives of the latter in 70–90% yield, i.e., there is apparently a transfer of the methyl anion from one *Co(III)* to another (41).

Some very interesting transalkylation reactions involving *Pd(II)* complexes have recently been discovered by Vol'pin and co-workers (175). $[\text{CH}_2=\text{CHCH}_2\text{Co}(\text{DMG})_2\text{py}]$ reacts with PdCl_4^{2-} in methanol at room temperature to give bis(π -allyl)palladium chloride. Solutions of Li_2PdCl_4 in methanol (or acetone, THF, MeCN, or HCONMe_2) will also catalyze the transfer of methyl from methyl-*Co*-salen, $(\text{DMG})_2$, and cobalamin complexes at 20°–25°C and even of phenyl from $[\text{PhCo}(\text{DMG})_2\text{py}]$ at 50°C to mono- and disubstituted olefins such as styrene, hexene, 1-octene, cyclohexene, vinyl acetate, and methyl acrylate. The reaction presumably occurs via the intermediate formation of a labile σ -organopalladium complex.



Several reactions of unknown mechanism with Pt and Au complexes are mentioned in Section C,3.

c. *Halogenating Agents*. Methyl-, propyl-, vinyl-, and α -pyridylpentacyanide complexes react with iodine to give methyl, propyl, and vinyl iodide and α -iodopyridine, respectively (74, 75, 109). 5-Deoxyadenosylcobalamin gives the alkyl iodide by reaction with either iodine or iodine monochloride (13). Other primary alkyl, isopropyl, phenyl, and acyl complexes have been reported to react with iodine (13, 64, 174), but the organic products have not been identified. It would appear that the reaction

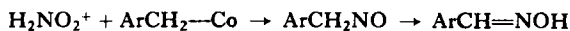


is a fairly general one, but no systematic study has been made and no kinetic data reported.

The complex [1-methylheptyl-Co(DMG)₂py] reacts with bromine in acetic acid to give 1-methylheptyl bromide together with some 1-octene and 2-octene dibromides but no 1-methylheptyl acetate, which suggests either that there are competing mechanisms or that the predominant mechanism is unusual (55).

The propylpentacyanide complex reacts with chlorine to form some propyl chloride (109).

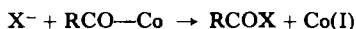
d. *Nitrosating Agents*. The reaction of nitrous acid with the three isomeric pyridiomethylpentacyanide complexes has been studied kinetically in aqueous perchloric acid (9). The reaction produces the oxime and the active species was identified as $H_2NO_2^+$.



The rates are very fast and comparable with those of diazotization reactions. They vary with the nature of the isomer in the order 3 > 4 > 2.

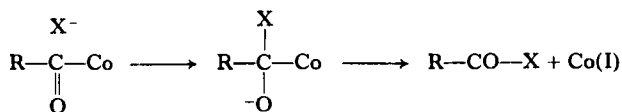
2. Transfer to Nucleophiles

The only definite examples are the acyl transfer reactions of acylcorrinoids, discovered by Bernhauer and Irion (14), and later studied in more detail by Yamada *et al.* (180). These reactions can be written



where R can be $-CH_3$, $-CH_2NH_2$, or $-CH_2NHCOCH_3$, and X can be HO^- or $NHOH^-$ [see also the discussion in Chapter 13 of ref. (136)]. The

reaction presumably proceeds by the addition of the nucleophile to the α -carbon to give an intermediate, which rapidly eliminates Co(I), i.e.,

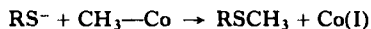


Fukui *et al.* have found that acetylcobinamide reacts faster than the cobalamin with hydroxide ($t_{1/2} = 4$ and 30 min, respectively, in 0.05 *N* KOH) (67). It is not known whether the cobinamide is five- or six-coordinate, but these relative rates establish the labilizing effect of the trans-axial ligand for heterolysis to give Co(I) as H_2O or none $> 5,6$ -dimethylbenziminazole (see also Section B,3).

Reactions which apparently involve transfer to nucleophiles such as thiols, cyanide, Grignard reagents, etc., are discussed in the next section.

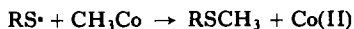
3. Transfer Reactions of Unknown Mechanism

Enzymatic methylation of homocysteine ($\text{HSCH}_2\text{CH}_2\text{CHNH}_2\text{COOH}$) by methylcobalamin to give methionine ($\text{CH}_3\text{SCH}_2\text{CH}_2\text{CHNH}_2\text{COOH}$) was discovered in 1962 by Woods and co-workers, who also noticed the occurrence of a much slower, nonenzymatic reaction giving the same products. Methylcobinamide showed the same activity as the cobalamin in both the enzymatic and nonenzymatic reactions (72, 71). It was subsequently discovered that HS^- , MeS^- , PhS^- , and $n\text{-BuS}^-$ will dealkylate a variety of methyl complexes [DMG, DMG-BF_2 , DPG, G, salen, (DO)(DOH)pn, cobalamin] and even ethyl- Co(DMG)_2 complexes to give the thioethers, and it was suggested that the reaction involved transfer of the carbonium ion to the attacking thiolate (161, 164), e.g.,



However, more recent work has shown that the reaction of thioglycolic acid (HSCH_2COOH) with methylcobalamin to give the methyl thioether requires oxygen and shows an induction period [which can be reduced by increasing the pH, the thiol concentration, or the partial pressure of O_2 , and eliminated by the addition of the Co(II) complex], followed by a steady-state reaction [whose rate increases with pH, the concentration of the CH_3Co and Co(II) complexes and the partial pressure of O_2 , but is independent of thiol concentration]. Neither the induction period nor the steady-state

rate were affected by the addition of trace metals (3). This transfer reaction clearly cannot proceed by the simple mechanism given in the above equation. The simplest possible mechanism would involve attack by thiol radicals (formed in the autoxidation of thiols catalyzed by the simple Co(III) and Co(II) complexes), i.e.,



Other more complicated mechanisms are conceivable.

Other reactions which apparently involve transfer to nucleophiles include those of [MeCo(salen)] with MeMgI to give ethane as well as methane and H₂ (64), and of [MeCo(DMG)₂X] complexes with CN⁻ and PhNMe⁻, apparently to give MeCN and PhNMe₂ (161). The mechanisms of these processes have not been studied. Nevertheless it is known that the reaction of methyl- and ethylcobalamin with cyanide (products not known) requires oxygen, and shows an induction period [see Chapter 13 of ref. (136)].

The reaction of [MeCo(DMG)₂py] in DMF with 1,4-butanedithiol in an atmosphere of CO₂ produces small amounts (up to 1%) of acetic acid in addition to methane (157).

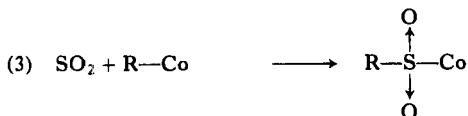
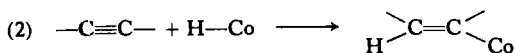
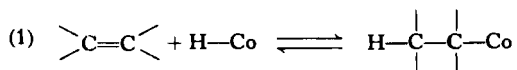
Several reactions involving metal ions are known which might involve the transfer of an alkyl radical. Rapid transfer of the alkyl group has been observed between [MeCo(BAE)H₂O] and [Co^{II}tfn] in both the forward and reverse directions, and from the ethyl, but not the pentafluoroethyl, analogue, and it was suggested that the reaction involved electron transfer accompanied by the transfer of the alkyl group (174a). Methyl chloride is formed by treating methylcobalamin with mixtures of PtCl₄²⁻ and PtCl₆²⁻ or of AuCl₂⁻ and AuCl₄⁻, but not with a single component alone, or with Fe(III) or [Fe(CN)₆]³⁻ in the presence of chloride ions (2).

D. Insertion and Elimination Reactions

As already pointed out, the presence of a macrocyclic ligand, which occupies the four equatorial coordination sites of an octahedral complex, will tend to limit insertion and elimination reactions of the Co—C bond to those which require only that single coordination site. The presence of unidentate ligands in the pentacyanides, on the other hand, will offer greater opportunities for reactions which require a second, adjacent site.

The following types of insertion and elimination reaction have been

observed with the macrocyclic (and, except for 4 and 5, with the pentacyanide) complexes:



No insertion or elimination of CO, i.e., reaction (6)



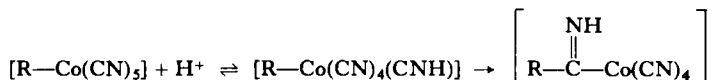
has yet been observed with any macrocyclic complex, but the insertion of CNH (isoelectronic with CO),



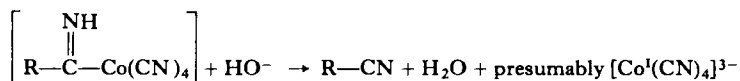
and perhaps also the elimination of CO, occur with the pentacyanides. Reactions (4) and (7) appear to be the first examples of the insertion of O₂ and CNH into transition metal-alkyl bonds. Of these reactions only (3), (4), (6), and (7) involve insertion into a Co—C bond. The addition of CoH to olefins and acetylenes has been discussed in Section III,A, the reverse elimination of olefins in Section B,1,f, and the insertion of CO into Co—OR in Section III,C.

Kwiatek and Seyler were the first to report that many organopentacyanides, when treated first with acid and then with alkali, liberate nitriles (110). This reaction occurs with unsubstituted primary and secondary alkyl, benzyl, vinyl, and phenyl complexes, while allyl, 2-oxo-, 2-hydroxy-, and 2-alkoxy complexes simply release the organo-ligand on treatment with acid, and 1-cyanoalkyl and α -pyridyl complexes are stable (105) (see also Table IV). The yield of nitrile is usually far from quantitative and is

accompanied by the formation of the corresponding acid and amide. The mechanism of this reaction was elucidated by Johnson, Tobe and, Wong in their kinetic study of the reactions of the 2-, 3-, and 4-pyridiomethylpentacyanides in perchloric acid at 25°–40° C (101). At pH < 1 one of the cyanides becomes protonated and the resultant complex undergoes rearrangement involving insertion of CNH into the cobalt–alkyl bond.



The rates of reaction vary with the isomer in the order 3 > 4 > 2. The imido complex may then be hydrolyzed under more vigorous acid conditions to give ammonium ion and the carboxylic acid, probably via the intermediate formation of the acyl complex. In this case the 2-isomer reacts more rapidly than the others. Treatment of the imido complexes with alkali, however, liberates the nitrile (see also Section B,1,e):

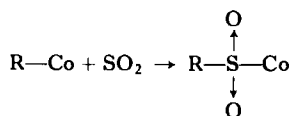


Similar reactions were also observed with the methyl- (101) and α -(2-pyridio)ethylpentacyanides (102), but in the latter case kinetic evidence was also obtained for insertion by the doubly protonated complex, viz., $[\text{RCo}(\text{CN})_3(\text{CNH})_2]$, as well as the singly protonated complex (102). Kwiatek reports that complexes containing groups very susceptible to rearrangement (such as neophyl) yield the unrearranged nitrile, indicating that the alkyl group remains bound in the complex during these reactions (105). Kinetic studies establish the presence of one or more CNH ligands in the complex which undergoes rearrangement, but they cannot decide whether it is CN^- or CNH which undergoes insertion. The group CNH is, however, isoelectronic with CO, and the parallel between the insertion of CO and CNH is striking. It should be mentioned that the pyridio methyl and ethyl complexes undergo a different type of reaction at pH 0–6, involving the loss of cyanide, followed probably by homolytic fission of the cobalt–alkyl bond (100–102) (see also Section B,1,a).

No insertion of CO into a Co–C bond has been reported, although possible equilibria and reactions involving CO at a pressure of 1 atm have been examined with DMG (163, 80), salen (44), and corrinoid complexes

(63, 66). However, vinylacetyl chloride ($\text{CH}_2=\text{CHCH}_2\text{COCl}$) reacts with $[\text{Co}(\text{CN})_5\text{H}]^{3-}$ to give propylene, presumably via the intermediate formation of the butenoyl complex ($\text{CH}_2=\text{CHCH}_2\text{COCo}$), which then eliminates CO to form the unstable allyl complex (111, 105). No test has apparently been made for the possible insertion of CO by organopentacyanides.

Yamamoto, Shono, and Shinra in 1967 (181) reported the reaction of the benzylpentacyanide with SO_2 to give the benzylsulfinate complex. Since then insertion reactions of the general type

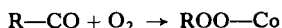


have been reported for $[\text{MeCo}(\text{CN})_5]^{3-}$ (98), $[\text{MeCo}(\text{BAE})\text{H}_2\text{O}]$ (98), $[\text{RCo}(\text{salen})\text{H}_2\text{O}]$, where R is Me and Et (128, 53, 98), $[\text{MeCo}(\text{saloph})\text{H}_2\text{O}]$ (53) and various DMG complexes where R is Me, Et, isopropyl, *sec*-octyl, and benzyl and X is py, isoquinoline, Me_2S , PPh_3 , and AsPh_3 (53, 98). With the latter complexes reaction was clearly slower with secondary than with primary alkyl groups (98). Reactions were usually carried out in liquid SO_2 at atmospheric pressure, less frequently in liquid SO_2 in a sealed tube at or above room temperature, by passing gaseous SO_2 into a solution of the complex, or by condensing SO_2 onto the solid complex. The products were identified as the *S*-sulfinate complexes by infrared and NMR spectroscopy and by synthesis via the reaction of RSO_2Cl with the Co(I) or Co—H complexes. No insertion occurred with aryl-salen or aryl-(DMG)₂ complexes even under forcing condition (53). Some of the DMG complexes show additional reactions with SO_2 , which probably involve coordination of SO_2 in the position trans to the sulfinate ligand (53, 98).

The sulfinate complexes do not lose SO_2 to reform the organocobalt complexes, even on heating (128, 53, 98). A thermogravimetric analysis of the compounds $\text{RSO}_2\text{Co}(\text{salen}), n\text{H}_2\text{O}$ (R = Me, Et, Ph, *p*-tolyl) showed peaks due to the removal of RSO_2 , while their mass spectra showed a very low abundance of the ions $\text{RCo}(\text{salen})^+$ (53). However, the decomposition of $[\text{PhCH}_2\text{Co}(\text{CN})_5]$ in aqueous solution at 100°C gives $\text{PhCH}_2\text{SO}_3\text{H}$ and $\text{PhCH}_2\text{CONH}_2$; the latter presumably results from elimination of SO_2 , followed by insertion of cyanide and hydrolysis (181).

Gaudemer and co-workers have reported both the photochemical (68) and thermal (58) insertion of O_2 into the Co—C bond of the complexes

[RCo(DMG)₂py] in solution in chloroform, acetone, or methanol according to the scheme.



Thermal insertion occurs at room temperature when R is XCH₂CHAr-, at 40° C when R is benzyl, allyl, or crotyl (in this case two isomeric peroxides are formed), but not even at 80° C when R is a simple primary alkyl group. The insertion of O₂ clearly involves prior dissociation of the Co—C bond to give more reactive species. The α -arylethyl complexes are known to decompose spontaneously into CoH and styrene derivatives (see Section B,1,f). Oxygen will presumably react with the hydride or Co(I) to give the hydroperoxide complex, which then adds to the styrene. The benzyl and allyl complexes appear to undergo homolytic fission to give Co(II) and free radicals (see Section B,1,a); in this case O₂ would react first with the radicals.

The insertion of O₂ occurs only after prior fission of the Co—C bond and requires only one coordination position. The insertion of CO into M—R bonds [see ref. (79)] and the insertion of CNH, however, both require two coordination positions. The insertion of SO₂ is of current interest (179). It has been shown that the mechanisms of insertion of CO and SO₂ are totally different. The insertion of CO into [Me₃CCHDCHDFe(CO)₂(C₅H₅)] involves retention of configuration at the α -carbon, while insertion of SO₂ involves ~80% inversion (177). The observation that the insertion of CNH (and possibly the elimination of CO) occurs with the pentacyanides, while neither the insertion nor elimination of CO occur with macrocyclic compounds, yet they can all undergo insertion of SO₂, again emphasizes the difference in mechanism between CO and SO₂. It has, in addition, been shown from the effect of substituents and bases on the rate that SO₂ reacts as an electrophile (179). Electrophilic attack, inversion, and the use of only one coordination site could all be explained by a mechanism involving transfer of a carbanion to the SO₂, which attacks from the side opposite to cobalt, to give an ion pair of five-coordinate Co(III) and the sulfinate anion, followed by rotation of the anion to form the new Co—S bond. This is analogous to the reaction with Br₂, which also involves inversion at the α -carbon (177). However, while Br₂ gives the uncharged RBr which diffuses away, SO₂ forms the negatively charged RSO₂⁻, which is held by electrostatic attraction to the positively charged metal until formation of the Co—S bond.

E. Oxidation and Reduction

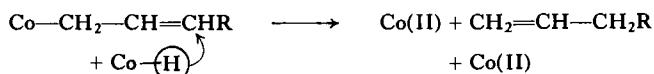
Organocobalt(III) complexes are stable towards oxygen unless they undergo spontaneous fission of the Co—C bond to give Co(II), Co(I), or CoH complexes (see Section VI,B,1,a and D). Reactions with halogens are dealt with in Section VI,C,1,c.

No systematic study has yet been made of reduction, but some interesting differences in reactivity are noticed. Reduction by borohydride leads to evolution of the hydrocarbon from $[\text{CH}_3\text{Co}(\text{BAE})]$ (49) and various unspecified DMG complexes (161) [though see ref. (147)], while alkyl- and benzylpentacyanides (109) and most organocobalamins are stable. Exceptions are cobalamins with the ligands $-\text{C}\equiv\text{CH}$, $-\text{CH}_2\text{COOH}$ ($\rightarrow\text{CH}_3\text{-COOH}$), $-\text{CH}_2\text{CF}_3$, and $-\text{CH}_2\text{SO}_3\text{H}$ [for references see Chapter 11 of ref. (136)]. On the other hand, the alkylcobalt(III) complexes $[\text{RCo}(\text{tim})\text{X}]$ and $[\text{RCo}(\text{CR})\text{X}]$, where R is methyl or benzyl and X is a halide ion, can be reduced by borohydride in methanol or by Na/Hg in acetonitrile to the alkylcobalt(I) complexes, which can be isolated and further alkylated to the *trans*-dialkylcobalt(III) complexes (60). The alkylcobalt(III) complexes $[\text{RCo}\{(\text{DO})(\text{DOH})\text{pn}\}\text{X}]$, where R is methyl, phenyl, or benzyl and X is H_2O or I^- , can also be reduced by borohydride in methanol, by CO in alkaline solution, or by Na/Hg in THF to organo-cobalt(I) complexes, which can be further alkylated to give *trans*-dialkylcobalt(III) complexes (45, 42).

Catalytic hydrogenation with platinum liberates the hydrocarbon from methylcobalamin (57) and from alkyl-Co-DMG complexes (161), but not from pentacyanides with primary alkyl, vinyl, or benzyl ligands, though the σ -allyl complex yields propylene (109). Sodium sand gives mixtures of hydrocarbons with the alkyl-Co-salen complexes (64). Dithioerythritol will liberate methane from a variety of methyl complexes [cobalamin, DMG, DMG-BF_2 , G, DPG, CHD, salen, and $(\text{DO})(\text{DOH})\text{pn}$] (156), as will 1,4-butanedithiol from the DMG complex (157), and certain unspecified thiols will reduce DMG complexes with substituted alkyl ligands (e.g., $\text{Co-CH}_2\text{COOH} \rightarrow \text{CH}_3\text{COOH}$) (163, 164). Reaction with thiols can also lead to the formation of thioethers (see Section C,3).

Most organopentacyanides are stable towards $[\text{Co}(\text{CN})_5\text{H}]^{3-}$, with the exception of allyl complexes which react to liberate propylene derivatives (105). This is one of the steps in the homogeneous hydrogenation of butadienes catalyzed by cobalt cyanide complexes (see Section VII,A).

It was suggested that reaction occurred by the transfer of a hydrogen atom to the γ -carbon of the allyl group, i.e.,



Methyl and other organo-DMG complexes react with the Co(I) complexes to liberate the hydrocarbon (161, 163).

For studies on polarographic reduction see, for example, ref. (91) (corrinoids), (161, 163) (DMG) and (51) (DMG, salen, BAE).

VII

CATALYTIC AND ENZYMATIC REACTIONS

The best known catalytic reactions are the homogeneous hydrogenations catalyzed by cobalt cyanide complexes (there are two different mechanisms, only one of which proceeds via the formation of an organocobalt complex) and the enzymatic reactions, which involve either isomerization (in this case the enzyme contains an organocobalt complex, but there is no evidence that the substrate forms an organocobalt complex) or the transfer of a methyl group (probably via the formation of a methylcobalt complex). A few other cobalt complexes have been reported to catalyze hydrogenations, and several cobalt complexes can catalyze the reduction of organic compounds by borohydride, etc. Cobalt cyanide complexes in the presence of hydrogen also catalyze H/D exchange (between organic compounds and the solvent or gas) and isomerization; but these reactions are usually observed merely as side reactions during hydrogenation. There is a need for a more systematic study of possible catalytic reactions other than the homogeneous hydrogenations catalyzed by cobalt cyanide complexes. The preferential reduction of $-\text{CCl}_2-$ groups to $-\text{CHCl}-$ by borohydride in the presence of vitamin B_{12} (12) and of $-\text{CCl}_3$ to CHCl_2 in the presence of Co(II) salen (116) is probably an indication of the type of reaction waiting to be discovered and perhaps developed for synthetic purposes.

A. Homogeneous Hydrogenation Catalyzed by Cobalt Cyanide Complexes

The cobalt cyanide complexes are excellent catalysts for the homogeneous hydrogenation at room temperature of a variety of organic (and inorganic)

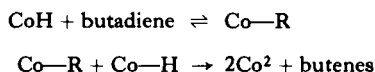
compounds, and these reactions have been extensively studied for their academic and potential industrial interest. There is probably no other catalyst which can hydrogenate such a wide range of substrates under such mild conditions. The homogeneous hydrogenation of isatin and cinnamic acid was discovered by Iguchi in 1942 (93). Since then the list has been extended to include the reduction of compounds such as organic halides to paraffins; diolefins and other conjugated olefins to olefins; styrene to ethylbenzene; α,β -unsaturated acids to saturated acids; benzaldehyde to benzyl alcohol; quinones to hydroquinones; epoxides to alcohols; nitrobenzene to azobenzene, hydrazobenzene, and aniline; oximes to amines; ketones with ammonia to amines. Small differences in structure can cause large differences in the ease of reduction, e.g., crotonaldehyde and methacrylic acid are reduced at room temperature, but crotonic acid, methacrolein, acrylic acid, and acrolein are not, while styrene derivatives ($\text{PhCH}=\text{CHR}$) are reduced when R is H or CH_2OH but not CH_3 (107). Kwiatak (105) has reviewed the literature up to 1967. For additional more recent examples of catalytic hydrogenation by cobalt cyanide complexes see refs. (10, 132, 108, 103). In most cases hydrogenation proceeds readily at room temperature and a pressure of 1 atm of hydrogen. The reactions are usually carried out in aqueous or methanolic solutions, in which the cobalt complexes are soluble, but two-phase systems can be used, e.g., in the hydrogenation of styrene or benzoquinone dissolved in benzene.

The main initial complex formed on mixing solutions of, for example, cobalt chloride and potassium cyanide, is the five-coordinate $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ (141), which is hereafter written Co^2 . This rapidly adsorbs H_2 to give $[\text{Co}^{\text{III}}(\text{CN})_5\text{H}]^{3-}$ as the major product (6). This hydride (written $\text{Co}-\text{H}$) is considered to be the real hydrogenating agent and behaves as though it were a source of hydrogen atoms. There are two different mechanisms for the homogeneous hydrogenation of organic compounds catalyzed by cobalt cyanide complexes. The first mechanism (I), proposed by Kwiatak (107) for the hydrogenation of butadiene to butenes, involves the intermediate formation of an organocobalt complex, which reacts with $\text{Co}-\text{H}$ to give the reduced product. The second mechanism (II), proposed by Simandi and Nagy (166) for the reduction of cinnamic acid, involves the intermediate formation of a free radical, which can then abstract a hydrogen atom from $\text{Co}-\text{H}$ to give the reduced product. For either mechanism the formation of a stable organocobalt complex which does not dissociate to give a radical or olefin and is not cleaved reductively by $\text{Co}-\text{H}$ is tantamount

to the "poisoning" of the catalyst, and the effects of small differences in structure on the reducibility of organic compounds are probably related mainly to the stability of the organocobalt complex. The evidence for and chief features of these mechanisms can be summarized as follows.

1. Mechanism I. Via an Organocobalt Complex

Butadiene reacts rapidly with 1 mole of Co—H, but not with Co², to give an organocobalt complex or complexes. These adducts will react directly with Co—H to form butenes, or decompose under nitrogen to give an equimolar mixture of butadiene and butenes. Reduction with D₂ showed that not only the butenes, but also recovered butadiene, contained some deuterium. Butenes, on the other hand, neither form adducts with Co—H or Co² nor undergo catalyzed exchange with D₂O (105). The formation of the organocobalt complex (Co—R) is therefore reversible, while the formation of butenes is irreversible, i.e.,



Variation of the CN/Co ratio brings about a striking change in the ratio of butene isomers produced (107, 170, 168). Compare, for example, the following percentages (107):

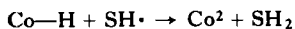
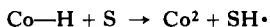
CN/Co	1-Butene	<i>trans</i> -2-butene	<i>cis</i> -2-butene
4.5	13	86	1
6.0	85	12	3

It was suggested that this change in product distribution was due to the existence of an equilibrium between two types of complex, viz., a σ -butenyl-pentacyanocobaltate(III) and a π -butenyltetracyanocobaltate(III) (107, 109). However, further study of the kinetics and product distribution suggested the presence of two σ -bonded complexes, viz., σ -but-1-en-3-yl and σ -but-2-en-1-yl (24a). Direct evidence for the existence of a cyanide-dependent equilibrium between the σ - and π -bonded organocyanide complexes has been obtained from NMR studies of the complex prepared by the reaction of allyl halides with Co—H (109) (see also Section V,C). Both butadiene and crotyl chloride react with Co—H to give the same

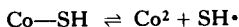
product, whose NMR spectrum is consistent with its formulation as the σ -but-2-en-1-yl complex, but the observation of any σ - π equilibrium is hindered by the decomposition of the complex (109). Attempts to isolate and study the adducts of other reducible conjugated olefins have failed (105). A similar high proportion of the terminal olefin is also found in the hydrogenation at high CN/Co ratios of isoprene (108, 171), 1,3-pentadiene (108), and 2,3-dimethylbutadiene (105). Evidence for the intermediate formation of organocobalt complexes is also provided by the stereospecificity observed in the hydrogenation of phenylethyne-carboxylic acid (10) and certain epoxides (106, 103) (see also Section III,A).

2. Mechanism II. Via a Free Radical

Simandi and Nagy studied the kinetics of the catalyzed hydrogenation of cinnamic acid (S) to dihydrocinnamic acid (SH₂) under steady-state conditions (166). They concluded that the kinetically important reactions were the two successive transfers of hydrogen atoms, viz.,

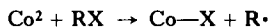


and that any scheme involving the direct reaction of Co—R (i.e., Co—SH) with Co—H was incompatible with their results. The intermediate formation of Co—SH in the reaction of Co—H with S cannot, however, be excluded on kinetic grounds. In fact, there probably exists a rapid and reversible equilibrium:

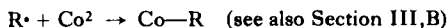
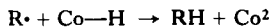


Evidence for the intermediate formation of a free radical comes from labeling experiments, which show that both reduction and isomerization, which sometimes proceeds concurrently, are nonstereospecific (94, 10).

The catalytic hydrogenation of alkyl halides (RX) probably also proceeds via the intermediate formation of free radicals, which are formed in this case by the abstraction of a halogen atom (see Section III,B).



The free radical can then react in several ways, e.g.,



Since organocobalt complexes containing primary alkyl (but excluding allyl—see above) or benzyl groups are stable to dissociation and to reduction by Co—H , their formation leads to poisoning of the system, and the degree of poisoning will depend on the relative rates of the above reactions. The hydrogenation of optically active 1-bromo-2,2-diphenylcyclopropanecarboxylic acid occurs with loss of activity, which shows that the reduction of alkyl halides, like that of α,β -unsaturated acids, is non-stereospecific and provides evidence for the intermediate formation of a free radical (108).

B. Other Catalytic Reductions and Hydrogenations

Only a few other cobalt complexes of the type covered in this review (and therefore excluding, for example, the cobalt carbonyls) have been reported to act as catalysts for homogeneous hydrogenation. The complex Co(DMG)_2 will catalyze the hydrogenation of benzil (PhCOCOPh) to benzoin (PhCHOHCOPh). When this reaction is carried out in the presence of quinine, the product shows optical activity. The degree of optical purity varies with the nature of the solvent and reaches a maximum of 61.5% in benzene. It was concluded that asymmetric synthesis occurred via the formation of an organocobalt complex in which quinine was coordinated in the trans position (133). Both Co(DMG)_2 and cobalamin-cobalt(II) in methanol will catalyze the following reductive methylations:



An intermediate could be isolated in the case of aniline and Co(DMG)_2 and indirect evidence suggested the presence of a $\text{PhNHCH}_2\text{—Co}$ bond (164, 165).

Many of these cobalt complexes will catalyze the reduction of organic compounds by borohydride, hydrazine, thiols, etc. Cobalt cyanide complexes will catalyze the reduction of α,β -unsaturated acids by borohydride (105); DMG complexes the reduction of butadiene and isoprene by borohydride, but not by H_2 (124); Co(II) salen, the reduction of CHCl_3 and CH_3CCl_3 to the dichloro compounds by borohydride (116); and cyanocobalamin, the selective reduction of $\text{—CCl}_2\text{—}$ by borohydride to —CHCl— in compounds such as aldrin, isodrin, dieldrin, and endrin without

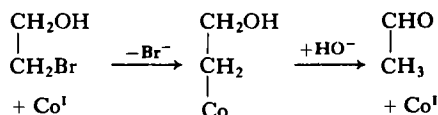
attacking either the olefinic bond or the epoxide rings (12). Cyanide complexes will also reduce butadiene to butenes in the absence of H_2 , but in the presence of CO_2 or various oxy acids (172, 173), and the reduction of atropic acid by cobalt cyanide complexes in the presence of *L*-isoleucine yields hydratropic acid showing slight optical rotation (133). For some other examples see ref. (105).

C. Exchange and Isomerization

H/D exchange and isomerization are sometimes observed as side reactions during hydrogenations catalyzed by cobalt cyanide complexes by either of the two mechanisms described in Section VII,A. As already mentioned, exchange occurs between butadiene and D_2O (107), presumably via the rearrangement of the σ - to the π -allylic type of complex. A reversible rearrangement of the σ -alkyl-Co(III) into the π -olefin-Co(I) complex (see Section V,C) probably explains the exchange of the protons in the organo-ligands in the complexes $[NCCH_2CHRCo(DMG)_2py]$, where $R = H$ or CN , and D_2O in the solvent mixture (159). The slow decomposition of α -(2-pyridio)ethylpentacyanocobaltate(III) in D_2O yields 2-vinylpyridine, in which only the terminal protons have exchanged, and 2-ethylpyridine, in which all three α -protons but only one of the two β -protons have exchanged. This probably occurs via the reversible addition of $[Co(CN)_5D]^{3-}$ to 2-vinylpyridine (102). The reduction of sorbic acid to 2- and 3-hexenoic acids is apparently accompanied by exchange on the δ -carbon atoms (117). Exchange will, of course, accompany isomerization, but slow exchange in the absence of any other complicating reactions has been observed at the β -position of 4,5,5-trimethylcyclopent-1-ene-4-dicarboxylic acid (94).

Isomerization has been observed with many α,β -unsaturated carboxylic acids such as *cis*-cinnamic (10), angelic, maleic, and itaconic acids (94). The possibility of catalyzing the interconversion of, for example, 2-ethylbutadiene and 3-methylpenta-1,3-diene has not apparently been explored. The cobalt cyanide hydride will also catalyze the isomerization of epoxides to ketones (even terminal epoxides give ketones, not aldehydes) as well as their reduction to alcohols. Since the yield of ketone increases with pH, it was suggested that reduction involved reaction with the hydride $[Co^{III}(CN)_5H]^{3-}$ and isomerization reaction with $[Co^I(CN)_5]$ (103). A related reaction is the decomposition of 2-bromoethanol to acetaldehyde

catalyzed by $[\text{Co}^{\text{I}}(\text{DMG})_2]^-$ in alkaline solution, for which the individual steps in the reaction are known (150).



It is interesting that some of the enzymatic reactions involve the rearrangement of diols to aldehydes (see below).

D. Enzymatic Reactions

The reactions which are catalyzed by enzymes containing cobalt corrinoids can be classified into three groups.

1. Transfer of Methyl Groups (See Table VI)

The corrinoids involved in methyl group transfer do not possess the organo-ligand 5'-deoxyadenosyl [see structure (II), Section I,B] and the reaction probably proceeds via the intermediate formation of the methyl cobalt complex, but no mechanistic details have yet been established.

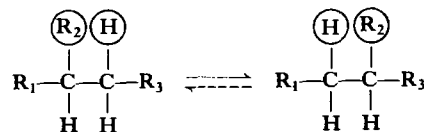
TABLE VI
METHYL TRANSFER REACTIONS CATALYSED BY CORRINOID-CONTAINING ENZYMES

Substrates		To	Product
From			
N ⁵ -Methyltetrahydrofolic acid Methylcobalamin ^a	Homocysteine		Methionine
N ⁵ -Methyltetrahydrofolic acid Various methylcorrinoids ^a CH ₃ OH	Various reducing agents		CH ₄
CH ₃ OH	B ₁₂ s		Methylcobalamin
N ⁵ -Methyltetrahydrofolic acid Methylcobalamin ^a	CO ₂ Hg ²⁺		CH ₃ COOH CH ₃ Hg ⁺

^a Free methylcorrinoids, i.e., not bound to the apoenzyme; these are not, of course, natural substrates.

Some analogous *in vitro* reactions of methylcobalt complexes are known, e.g., the methylation of thiols (see Section VI,C,3) and of mercury(II)

TABLE VII
 "ISOMERASE" REACTIONS CATALYZED BY ENZYMES CONTAINING 5'-DEOXYADENOSYLCORRINOIDS



Substrate	R ₁	R ₂	R ₃	Product
Irreversible reactions				
Ethane-1,2-diol	H	OH	OH	Acetaldehyde
Propane-1,2-diol	CH ₃	OH	OH	Propionaldehyde
Glycerol	HOCH ₂	OH	OH	β-Hydroxypropionaldehyde
Ethanolamine	H	NH ₂	OH	Acetaldehyde + NH ₃
3,6-Diaminohexanoate	H	NH ₂	-CH ₂ CHNH ₂ CH ₂ COOH	3,5-Diaminohexanoate
Reversible reactions				
L-Glutamate	H	-CHNH ₂ COOH	COOH	<i>threo</i> -β-methylaspartate
Succinyl-coenzyme A	H	-COSR	COOH	L-Methylmalonyl coenzyme A

ions (see Section VI,C,1,a). The sinister aspects of mercury pollution are due to the conversion of inorganic forms of mercury into the far more toxic methylmercury compounds by this reaction.

2. "Isomerase" Reactions (see Table VII)

The enzymes in the so-called "isomerase" reactions contain 5'-deoxyadenosylcorrinoids. Labeling experiments have been used to identify the C, H, and O atoms which have moved in the course of the rearrangement and to show that during the reaction the hydrogen atoms of the substrate exchange with the hydrogen atoms of the C-5' atom coordinated to the cobalt ion, but not with the solvent. There is also some spectroscopic evidence that the Co—C bond is broken during the reaction.

3. Ribonucleoside Triphosphate Reduction

The reduction of ribonucleoside triphosphates by various dithiols which are capable of intramolecular cyclization on oxidation (dihydrolipoate, dithioerythritol, dithiothreitol) yields 2'-deoxyribonucleoside triphosphates. These reactions also require 5-deoxyadenosylcorrinoids.

For further details and references see Chapter 17 of ref. (136).

REFERENCES

1. Adin, A., and Espenson, J. H., *Chem. Commun.* 653 (1971).
2. Agnes, G., Bendle, S., Hill, H. A. O., Williams, F. R., and Williams, R. J. P., *Chem. Commun.* 850 (1971).
3. Agnes, G., Hill, H. A. O., Pratt, J. M., Ridsdale, S. C., Kennedy, F. S., and Williams, R. J. P., *Biochim. Biophys. Acta* **252**, 207 (1971).
4. Bailey, N. A., Higson, B. M., and McKenzie, E. D., *Inorg. Nucl. Chem. Lett.* **7**, 591 (1971).
5. Baird, M. C., Hartwell, G., and Wilkinson, G., *J. Chem. Soc., A* 2037 (1967).
6. Banks, R. G., and Pratt, J. M., *J. Chem. Soc., A* 854 (1968).
7. Barnett, R., Hogenkamp, H. P. C., and Abeles, R. H., *J. Biol. Chem.* **241**, 1483 (1966).
8. Bartlett, E. H., and Johnson, M. D., *J. Chem. Soc., A* 517 (1970).
9. Bartlett, E. H., and Johnson, M. D., *J. Chem. Soc., A* 523 (1970).
10. Basters, J., van Bekkum, H., and van Reijen, L. L., *Rec. Trav.* **89**, 491 (1970).
11. Bayston, J. H., Beale, R. N., King, N. N., and Winfield, M. E., *Aust. J. Chem.* **16**, 954 (1963).
12. Bieniek, D., Mosa, D. N., Klein, W., and Korte, F., *Tetrahedron Lett.* 4055 (1970).
13. Bernhauer, K., and Irion, E., *Biochem. Z.* **339**, 521 (1964).
14. Bernhauer, K., and Irion, E., *Biochem. Z.* **339**, 530 (1964).
15. Bied-Charreton, C., and Gaudemer, A., *C. R. Acad. Sci. Ser. C* **272**, 1241 (1971).
16. Bigotto, A., Costa, G., Mestroni, G., Pellizer, G., Puxeddu, A., Reisenhofer, E., Stefani, L., and Tauscher, G., *Inorg. Chim. Acta* **4**, 41 (1970).

17. Booth, G., Craig, P. J., Dobbs, B., Pratt, J. M., Randall, G. L. P., and Williams, A. G., *J. Chem. Soc., A* 1964 (1971).
18. Borodulina-Shvets, V. I., Rudakova, I. P., Dymova, S. F., and Yurkevich, A. M., *J. Gen. Chem. USSR* **40**, 676 (1970).
19. Brodie, J. D., *Proc. Nat. Acad. Sci. U.S.* **62**, 461 (1969).
20. Brodie, J. D., and Poe, M., *Biochemistry* **10**, 914 (1971).
21. Brückner, S., Calligaris, M., Nardin, G., and Randaccio, L., *Inorg. Chim. Acta* **2**, 416 (1968).
22. Brückner, S., Calligaris, M., Nardin, G., and Randaccio, L., *Inorg. Chim. Acta* **3**, 278 (1969).
23. Brückner, S., Calligaris, M., Nardin, G., and Randaccio, L., *Inorg. Chim. Acta* **3**, 308 (1969).
24. Brückner, S., Calligaris, M., Nardin, G., and Randaccio, L., *Chem. Commun.* 152 (1970).
- 24a. Burnett, M. G., Connolly, P. J., and Kemball, C., *J. Chem. Soc. A* 991 (1968).
25. Busch, D. H., Weber, J. H., Williams, D. H., and Rose, N. J., *J. Amer. Chem. Soc.* **86**, 5161 (1964).
26. Calderazzo, F., and Floriani, C., *Chem. Commun.* 139 (1967).
27. Calligaris, M., Minichelli, D., Nardin, G., and Randaccio, L., *J. Chem. Soc., A* 2720 (1971).
28. Calligaris, M., Nardin, G., and Randaccio, L., *Chem. Commun.* 1248 (1969).
29. Calligaris, M., Nardin, G., and Randaccio, L., *Chem. Commun.* 1079 (1970).
30. Cesari, M., Neri, C., Perego, G., Perrotti, E., and Zazzetta, A., *Chem. Commun.* 276 (1970).
31. Chatt, J., and Shaw, B. L., *J. Chem. Soc.* 285 (1961).
32. Chock, P. B., and Halpern, J., *J. Amer. Chem. Soc.* **91**, 582 (1969).
33. Clarke, D. A., Dolphin, D., Grigg, R., Johnson, A. W., and Pinnock, H. A., *J. Chem. Soc., C* 881 (1968).
34. Clarke, D. A., Grigg, R., Johnson, A. W., and Pinnock, H. A., *Chem. Commun.* 309 (1967).
35. Cockle, S., Hill, H. A. O., Williams, R. J. P., Mann, B. E., and Pratt, J. M., *Biochim. Biophys. Acta* **215**, 415 (1970).
36. Cope, A. C., and Gourlay, R. N., *J. Organometal. Chem.* **8**, 527 (1967).
37. Costa, G., and Mestroni, G., *Tetrahedron Lett.* 1781 (1967).
38. Costa, G., and Mestroni, G., *Tetrahedron Lett.* 1783 (1967).
39. Costa, G., and Mestroni, G., *Tetrahedron Lett.* 4005 (1967).
40. Costa, G., and Mestroni, G., *J. Organometal. Chem.* **11**, 325 (1968).
41. Costa, G., Mestroni, G., and Cocevar, C., *Chem. Commun.* 706 (1971).
42. Costa, G., Mestroni, G., Licari, T., and Mestroni, E., *Inorg. Nucl. Chem. Lett.* **5**, 561 (1969).
43. Costa, G., Mestroni, G., and Pellizer, G., *J. Organometal. Chem.* **11**, 333 (1968).
44. Costa, G., Mestroni, G., and Pellizer, G., *J. Organometal. Chem.* **15**, 187 (1968).
45. Costa, G., Mestroni, G., Pellizer, G., Tauzher, G., and Licari, T., *Inorg. Nucl. Chem. Lett.* **5**, 515 (1969).
46. Costa, G., Mestroni, G., and de Savorgnani, E., *Inorg. Chim. Acta* **3**, 323 (1969).
47. Costa, G., Mestroni, G., and Stefani, L., *J. Organometal. Chem.* **7**, 493 (1967).
48. Costa, G., Mestroni, G., Tauzher, G., Goodall, D. M., Green, M., and Hill, H. A. O., *Chem. Commun.* 34 (1970).
49. Costa, G., Mestroni, G., Tauzher, G., and Stefani, L., *J. Organometal. Chem.* **6**, 181 (1966).

50. Costa, G., Puxeddu, A., and Reisenhofer, E., *Chem. Commun.* 993 (1971).
51. Costa, G., Puxeddu, A., and Tazdher, G., *Inorg. Nucl. Chem. Lett.* **4**, 319 (1968).
52. Crumbliss, A. L., and Wilmarth, W. K., *J. Amer. Chem. Soc.* **92**, 2593 (1970).
53. Cozens, R. J., Deacon, G. B., Felder, P. W., Murray, K. S., and West, B. O., *Aust. J. Chem.* **23**, 481 (1970).
54. Day, P., Hill, H. A. O., and Price, M. G., *J. Chem. Soc., A* 90 (1968).
55. Dodd, D., and Johnson, M. D., *Chem. Commun.* 571 (1971).
56. Dolphin, D., and Johnson, A. W., *Chem. Commun.* 494 (1965).
57. Dolphin, D., Johnson, A. W., and Rodrigo, R., *Ann. N.Y. Acad. Sci.* **112**, 590 (1964).
58. Duong, K. N. V., Fontaine, C., Giannotti, C., and Gaudemer, A., *Tetrahedron Lett.* 118 (1971).
59. Duong, K. N. V., and Gaudemer, A. *J. Organometal. Chem.* **22**, 473 (1970).
60. Farmery, K., and Busch, D., *Chem. Commun.* 1091 (1970).
61. Firth, R. A., Hill, H. A. O., Mann, B. E., Pratt, J. M., Thorp, R. G., and Williams, R. J. P., *J. Chem. Soc., A* 2419 (1968).
62. Firth, R. A., Hill, H. A. O., Pratt, J. M., Thorp, R. G., and Williams, R. J. P., *J. Chem. Soc., A* 2428 (1968).
63. Firth, R. A., Hill, H. A. O., Pratt, J. M., Thorp, R. G., and Williams, R. J. P., *J. Chem. Soc., A* 381 (1969).
64. Floriani, C., Puppis, M., and Calderazzo, F., *J. Organometal. Chem.* **12**, 209 (1968).
65. Friedrich, W., and Nordmeyer, J. P., *Z. Naturforsch., B* **24**, 588 (1969).
66. Friedrich, W., and Messerschmidt, R., *Z. Naturforsch., B* **24**, 465 (1969).
67. Fukui, S., Shimizu, S., Yamada, R., and Umetani, T., *Vitamins* **40**, 113 (1969).
68. Giannotti, C., Gaudemer, A., and Fontaine, C., *Tetrahedron Lett.* 3209 (1970).
69. Golding, B. T., Holland, H. L., Horn, U., and Sakriker, S., *Angew. Chem., Int. Ed. Engl.* **9**, 959 (1970).
70. Griffith, W. P., and Wilkinson, G., *J. Chem. Soc.* 1629 (1959).
- 70a. Green M., Mawby, R. J., and Swinden, G., *Chem. Commun.* 127 (1967).
71. Guest, J. R., Friedman, S., Dilworth, M. J., and Woods, D. D., *Ann. N.Y. Acad. Sci.* **112**, 774 (1964).
72. Guest, J. R., Friedman, S., Woods, D. D., and Smith, E. L., *Nature (London)* **195**, 340 (1962).
73. Haim, A., and Wilmarth, W. K., *J. Amer. Chem. Soc.* **83**, 509 (1961).
74. Halpern, J., and Maher, J. P., *J. Amer. Chem. Soc.* **86**, 2311 (1964).
75. Halpern, J., and Maher, J. P., *J. Amer. Chem. Soc.* **87**, 5361 (1965).
76. Hanzlik, J., and Vlček, A. A., *Chem. Commun.* 47 (1969).
77. Hayward, G. C., Hill, H. A. O., Pratt, J. M., Vanston, N., and Williams, R. J. P., *J. Chem. Soc.* 6485 (1965).
78. Hayward, G. C., Hill, H. A. O., Pratt, J. M., and Williams, R. J. P., *J. Chem. Soc., A* 196 (1971).
79. Heck, R. F., *Advan. Chem. Ser. No.* **49**, 181 (1965).
80. Herlinger, A. W., and Brown, T. L., *J. Amer. Chem. Soc.* **93**, 1790 (1971).
81. Hieber, W., Vohler, G., and Braun, G., *Z. Naturforsch., B* **13**, 192 (1958).
- 81a. Hill, H. A. O., and Morallee, K. G., *J. Chem. Soc., A* 554 (1969).
82. Hill, H. A. O., Morallee, K. G., and Pellizer, G., *J. Chem. Soc., A* 209 (1969).
83. Hill, H. A. O., Morallee, K. G., Pellizer, G., Mestroni, G., and Costa, G., *J. Organometal. Chem.* **11**, 167 (1968).
84. Hill, H. A. O., Pratt, J. M., Ridsdale, S., Williams, F. R., and Williams, R. J. P., *Chem. Commun.* 341 (1970).
85. Hill, H. A. O., Pratt, J. M., and Williams, R. J. P., *J. Theor. Biol.* **3**, 423 (1962).

86. Hill, H. A. O., Pratt, J. M., and Williams, R. J. P., *J. Chem. Soc.* 5149 (1964).
87. Hill, H. A. O., Pratt, J. M., and Williams, R. J. P., *Chem. Ind. (London)* 197 (1964).
88. Hill, H. A. O., Pratt, J. M., and Williams, R. J. P., in "Methods in Enzymology," Vol. 18; Vitamins and Coenzymes, Part C (D. B. McCormick and L. D. Wright, eds.), p.5. Academic Press, New York, 1971.
89. Hogenkamp, H. P. C., *Federation Proc.* **25**, 1623 (1966).
90. Hogenkamp, H. P. C., *Annu. Rev. Biochem.* **37**, 225 (1968).
91. Hogenkamp, H. P. C., and Holmes, S., *Biochemistry* **9**, 1886 (1970).
- 91a. Hogenkamp, H. P. C., Rush, J. E., and Swenson, C. A., *J. Biol. Chem.* **240**, 3641 (1965).
92. Iguchi, M., *J. Chem. Soc. Jap.* **63**, 634 (1942).
93. Iguchi, M., *J. Chem. Soc. Jap.* **63**, 1752 (1942).
94. Jackman, L. M., Hamilton, J. A., and Lawlor, J. M., *J. Amer. Chem. Soc.* **90**, 1914 (1968).
95. Jensen, F. R., Madan, V., and Buchanan, D. H., *J. Amer. Chem. Soc.* **92**, 1414 (1970).
96. Johnson, A. W., and Kay, I. T., *J. Chem. Soc.* 2979 (1960).
97. Johnson, A. W., Mervyn, L., Shaw, N., and Smith, E. L., *J. Chem. Soc.* 4146 (1963).
98. Johnson, M. D., and Lewis, G. J., *J. Chem. Soc., A* 2153 (1970).
99. Johnson, M. D., and Mayle, C., *Chem. Commun.* 192 (1969).
100. Johnson, M. D., Tobe, M. L., and Wong, L. Y., *J. Chem. Soc., A* 491 (1967).
101. Johnson, M. D., Tobe, M. L., and Wong, L. Y., *J. Chem. Soc., A* 923 (1968).
102. Johnson, M. D., Tobe, M. L., and Wong, L. Y., *J. Chem. Soc., A* 929 (1968).
103. Kim, J. Y., and Kwan, T., *Chem. Pharm. Bull.* **18**, 1040 (1970).
104. Kundo, N. N., and Keier, N. P., *Kinet. Catal. (USSR)* **10**, 117 (1969).
105. Kwiatek, J., *Catal. Rev.* **1**, 37 (1967).
106. Kwiatek, J., Mador, I. L., and Seyler, J. K., *J. Amer. Chem. Soc.* **84**, 304 (1962).
107. Kwiatek, J., Mador, I. L., and Seyler, J. K., *Advan. Chem. Ser. No.* **37**, 201 (1963).
108. Kwiatek, J., and Seyler, J. K., *Advan. Chem. Ser. No.* **70**, 207 (1968).
109. Kwiatek, J., and Seyler, J. K., *J. Organometal. Chem.* **3**, 421 (1965).
110. Kwiatek, J., and Seyler, J. K., *J. Organometal. Chem.* **3**, 433 (1965).
111. Kwiatek, J., and Seyler, J. K., *Proc. 8th Int. Conf. Coord. Chem., Vienna* p. 308 (1964).
112. Lenhert, P. G., *Chem. Commun.* 980 (1967).
113. Lenhert, P. G., personal communication (1972).
114. Lenhert, P. G., *Proc. Roy. Soc. Ser. A* **303**, 45 (1968).
115. Lenhert, P. G., and Hodgkin, D. C., *Nature (London)* **192**, 937 (1961).
116. Levitin, I. Ya., Dvolaitzky, M., and Vol'pin, M. E., *J. Organometal. Chem.* **31**, C37 (1971).
- 116a. Ludwick, L. H., and Brown, T. L., *J. Amer. Chem. Soc.*, **91** 5188 (1969).
117. Mabrouk, A. F., Selke, E., Rohwedder, W. K., and Dutton, H. J., *J. Amer. Oil. Chem. Soc.* **42**, 432 (1965).
- 117a. McBride, B. C., Wood, J. M., Sibert, J. W., and Schrauzer, G. N., *J. Amer. Chem. Soc.* **90**, 5276 (1968).
118. Marzilli, L. G., Marzilli, P. A., and Halpern, J., *J. Amer. Chem. Soc.* **92**, 5752 (1970).
119. Marzilli, L. G., Marzilli, P. A., and Halpern, J., *J. Amer. Chem. Soc.* **93**, 1374 (1971).
120. Mason, R., and Russell, D. R., *Chem. Commun.* 182 (1965).
121. Mays, M. J., and Wilkinson, G., *J. Chem. Soc.* 6629 (1965).
122. Mays, M. J., and Wilkinson, G., *Nature (London)* **203**, 1167 (1964).
123. Mestroni, G., Camus, A., and Mestroni, E., *J. Organometal. Chem.* **24**, 775 (1970).
124. Mizuta, T., and Kwan, T., *Nippon Kagaku Zasshi* **88**, 471 (1967).

125. Mizuta, T., Suzuki, T., and Kwan, T., *Nippon Kagaku Zasshi* **88**, 573 (1967).
126. Müller, O., and Müller, G., *Biochem. Z.* **337**, 179 (1963).
127. Murakami, M., Kawai, R., and Suzuki, K., *Nippon Kagaku Zasshi* **84**, 669 (1963).
128. Murray, K. S., Cozens, R. J., Deacon, G. B., Felder, P. W., and West, B. O., *Inorg. Nucl. Chem. Lett.* **4**, 705 (1968).
129. Naumberg, M., Duong, K. N. V., and Gaudemer, A., *J. Organometal. Chem.* **25**, 231 (1970).
130. Ochiai, E., and Busch, D. H., *Chem. Commun.* 905 (1968).
131. Ochiai, E., Long, K. M., Sperati, C. R., and Busch, D. H., *J. Amer. Chem. Soc.* **91**, 3201 (1969).
132. Ohgo, Y., Takeuchi, S., and Yoshimura, J., *Bull. Chem. Soc. Jap.* **43**, 505 (1970).
133. Ohgo, Y., Takeuchi, S., and Yoshimura, J., *Bull. Chem. Soc. Jap.* **44**, 583 (1971).
134. Pailles, W. H., and Hogenkamp, H. P. C., *Biochemistry* **7**, 4160 (1968).
135. Poddar, S. N., and Biswas, D. K., *J. Inorg. Nucl. Chem.* **31**, 565 (1969).
136. Pratt, J. M., "The Inorganic Chemistry of Vitamin B₁₂." Academic Press, New York, 1972.
137. Pratt, J. M., *Accounts Chem. Res.* to be published.
138. Pratt, J. M., unpublished results.
139. Pratt, J. M., and Thorp, R. G., *Advan. Inorg. Chem. Radiochem.* **12**, 375 (1969).
140. Pratt, J. M., and Whitear, B. R. D., *J. Chem. Soc., A* 252 (1971).
141. Pratt, J. M., and Williams, R. J. P., *J. Chem. Soc., A* 1291 (1967).
142. Roshchupkina, O. S., Rudakova, I. P., Pospelova, T. A., Yurkevich, A. M., and Borod'ko, Yu. G., *J. Gen. Chem. USSR* **40**, 432 (1970).
143. Sakurai, T., Fox, J. P., and Ingraham, L. L., *Inorg. Chem.* **10**, 1105 (1971).
144. Schneider, P. W., Phelan, P. F., and Halpern, J., *J. Amer. Chem. Soc.* **91**, 77 (1969).
145. Schrauzer, G. N., *Accounts Chem. Res.* **1**, 97 (1968).
146. Schrauzer, G. N., *Inorg. Syn.* **11**, 61 (1968).
147. Schrauzer, G. N., and Deutsch, E., *J. Amer. Chem. Soc.* **91**, 3341 (1969).
148. Schrauzer, G. N., Deutsch, E., and Windgassen, R. J., *J. Amer. Chem. Soc.* **90**, 2441 (1968).
149. Schrauzer, G. N., and Holland, R. J., *J. Amer. Chem. Soc.* **93**, 1505 (1971).
150. Schrauzer, G. N., Holland, R. J., and Seck, J. A., *J. Amer. Chem. Soc.* **93**, 1503 (1971).
151. Schrauzer, G. N., and Kohnle, J., *Chem. Ber.* **97**, 3056 (1964).
152. Schrauzer, G. N., and Kratel, G., *Angew. Chem.* **77**, 130 (1965).
153. Schrauzer, G. N., and Kratel, G., *Chem. Ber.* **102**, 2392 (1969).
154. Schrauzer, G. N., Lee, L. P., and Sibert, J. W., *J. Amer. Chem. Soc.* **92**, 2997 (1970).
155. Schrauzer, G. N., and Sibert, J. W., *J. Amer. Chem. Soc.* **92**, 1022 (1970).
156. Schrauzer, G. N., and Sibert, J. W., *J. Amer. Chem. Soc.* **92**, 1421 (1970).
157. Schrauzer, G. N., and Sibert, J. W., *J. Amer. Chem. Soc.* **92**, 3509 (1970).
158. Schrauzer, G. N., Sibert, J. W., and Windgassen, R. J., *J. Amer. Chem. Soc.* **90**, 6681 (1968).
159. Schrauzer, G. N., Weber, J. H., and Beckham, T. M., *J. Amer. Chem. Soc.* **92**, 7078 (1970).
160. Schrauzer, G. N., Weber, J. H., Beckham, T. M., and Ho, R. K. Y., *Tetrahedron Lett.* 275 (1971).
161. Schrauzer, G. N., and Windgassen, R. J., *J. Amer. Chem. Soc.* **88**, 3738 (1966).
162. Schrauzer, G. N., and Windgassen, R. J., *J. Amer. Chem. Soc.* **89**, 143 (1967).
163. Schrauzer, G. N., and Windgassen, R. J., *J. Amer. Chem. Soc.* **89**, 1999 (1967).
164. Schrauzer, G. N., and Windgassen, R. J., *J. Amer. Chem. Soc.* **89**, 3607 (1967).

165. Schrauzer, G. N., and Windgassen, R. J., *Nature (London)* **214**, 492 (1967).
166. Simandi, L., and Nagy, F., *Acta Chem. Hung.* **46**, 137 (1965).
167. Smith, E. L., Mervyn, L., Muggleton, P. W., Johnson, A. W., and Shaw, N., *Ann. N. Y. Acad. Sci.* **112**, 565 (1964).
168. Spencer, M. S., and Dowden, D. A., British Patent, 882,686 (1959).
169. Suzuki, T., and Kwan, T., *Nippon Kagaku Zasshi* **86**, 713 (1965).
170. Suzuki, T., and Kwan, T., *Nippon Kagaku Zasshi* **86**, 1198 (1965).
171. Suzuki, T., and Kwan, T., *Nippon Kagaku Zasshi* **86**, 1341 (1965).
172. Suzuki, T., and Kwan, T., *Nippon Kagaku Zasshi* **87**, 926 (1966).
173. Suzuki, T., and Kwan, T., *Nippon Kagaku Zasshi* **88**, 400 (1967).
174. Taube, M., Dreves, H., and Duc-Hiep, T., *Z. Chem.* **9**, 115 (1969).
- 174a. van den Bergen, A., and West, B. O., *Chem. Commun.* 52 (1971).
175. Vol'pin, M. E., Volkova, L. G., Levitin, I. Ya., Boronina, N. N., and Yurkevich, A. M., *Chem. Commun.* 849 (1971).
176. Wagner, F., and Bernhauer, K., *Ann. N. Y. Acad. Sci.* **112**, 580 (1964).
177. Whitesides, G. M., and Buschetto, D. J., *J. Amer. Chem. Soc.* **93**, 1529 (1971).
178. Wilke, G., Bogdanovic, B., Hardt, P., Heimbach, P., Keim, W., Kröner, M., Oberkirch, W., Tanaka, K., Steinrücke, E., Watter, D., and Zimmermann, H., *Angew. Chem. Int. Ed. Engl.* **5**, 151 (1966).
179. Wojcicki, A., *Accounts Chem. Res.* **4**, 344 (1971).
180. Yamada, R., Umetani, T., Shimizu, S., and Fukui, S., *J. Vitaminol.* **14**, 316 (1968).
181. Yamamoto, K., Shono, T., and Shinra, K., *J. Chem. Soc. Jap.* **88**, 958 (1967).
182. Yamazaki, H., and Hagihara, N., *Bull. Chem. Soc. Jap.* **38**, 2212 (1965).
183. Yurkevich, A. M., Rudakova, I. N., and Preobrazhenskii, H. A., *Chem. Natur. Prod.* **3**, 41 (1967).
184. Zagalak, B., *Acta Biochim. Pol.*, **10**, 387 (1963).

The Literature of Organo-Transition Metal Chemistry 1971

M. I. BRUCE

*Department of Inorganic Chemistry
The University
Bristol, England*

A.	New Textbooks	448
B.	Reviews	450
C.	Primary Journals	451
D.	Abstracting Journals	451
E.	Conferences	451
F.	Synthesis	454
G.	Data Compilations	454
	Reference	455
	Appendix	455

In the previous volume of this series, an article entitled "Organo-Transition Metal Chemistry—A Guide to the Literature 1950–1970" (1) attempted to list a majority of the textual sources of information concerning transition metal organometallics which have appeared over the last two decades. Since the preparation of that survey, a large number of important new contributions have appeared. In the present account, the new review literature has been surveyed up to the end of 1971. In addition, several books and articles omitted from the earlier survey are included.

As mentioned briefly in the earlier volume, the most important new developments have been the publication of the first volumes in two series devoted in the main to various aspects of organometallic chemistry, and the production of a volume supplementary to the main Gmelin treatment of inorganic chemistry, solely concerned with the organic derivatives of vanadium and chromium. Unfortunately, the primary literature continues to increase and diversify, several new journals making their first appearance and including papers of interest to organometallic chemists. One contraction, at least in name, has been the absorption of *Organometallic Chemistry Reviews* into the *Journal of Organometallic Chemistry*. However, this now results in the latter journal being published in some ten volumes of about 500 pages each, at a price which puts it quite out of reach of all but the most wealthy individuals.

The past year has seen two important International Conferences devoted either entirely or in part to organometallic chemistry. These were the 5th International Conference on Organometallic Chemistry, held in Moscow, USSR, and the 23rd IUPAC Conference, at Boston, Massachusetts.

The second edition of the well-known "Red Book," the definitive recommendations of the IUPAC Commission on Nomenclature of Inorganic Chemistry, appeared in *Pure Appl. Chem.*, **28**, 1-110 (1971). It is also available separately as a hard-bound reprint. In this edition, the rules for naming organometallic compounds have been completely revised and extended, with introduction of the η nomenclature for organic ligands.

A. New Textbooks

This section lists a number of new books dealing either wholly or in part with organo-transition metal chemistry. Reference numbers follow those in the list given in reference (I).

- A60. J. P. Candlin, K. A. Taylor, and D. T. Thompson, "Reactions of Transition-Metal Complexes." Elsevier, Amsterdam, 1968. A review of types of reactions of metal complexes (e.g., substitution, combination, redox); reactions with various reagents (e.g., hydrocarbons, halides, carbon monoxide, and isonitrile); and preparation of new stabilised organic systems (e.g., metallocenes, carbenes). Intended for research workers, consequently written at a fairly high level, with emphasis on organometallics.
- A61. H. J. Keller, "NMR-Untersuchungen an Komplexverbindungen." Springer, Berlin, 1970. Expansion of review article 37.1.
- A62. A. N. Nesmeyanov, "Khimiya ferrotsena." Nauka, Moscow, 1969. Collection of 127 of the author's published papers on ferrocene chemistry.
- A63. E. W. Neuse and H. Rosenberg, "Metallocene Polymers." Dekker, New York, 1970. Comprehensive survey of metallocene macromolecules.
- A64. O. N. Temkin and R. M. Flid, "Kataliticheskie prevrashcheniya atsetilenovykh soedinenii v rastvorakh kompleksov metallov." (Catalytic conversion of acetylenic compounds in solutions of metal complexes.) Nauka, Moscow, 1968.
- A65. N. N. Korneev, "Complex Organometallic Catalysts," translated from the Russian original by Israel Program for Scientific Translations, Jerusalem, 1971.
- A66. L. Malatesta and F. Bonati, "Isocyanide Complexes of Metals." Wiley (Interscience), New York, 1969. Expansion and updating of review article 43.6.
- A67. V. I. Lyubimov, "Biokhimiya Fiksatsii Molekulyarnogo Azota" (Biochemistry of the fixation of molecular nitrogen). Nauka, Moscow, 1960.

Two publishers have commenced publication of a series of texts concerned with various aspects of organometallic chemistry, and the volumes which are currently available follow.

"Organometallic Chemistry," a series of monographs. Series editors, P. M. Maitlis, F. G. A. Stone, and R. West. Academic Press, New York.

- A68. B. G. Ramsey, "Electronic Transitions in Organometalloids," 1969. Confined to electronic spectra of Main Group Organometallics.
- A69. R. C. Poller, "The Chemistry of Organotin Compounds," 1970.
- A51. R. N. Grimes, "Carboranes," 1970.
- A70. P. M. Maitlis, "The Organic Chemistry of Palladium," 1971.
 - 70.1 Volume 1, Metal Complexes. Describes the organopalladium complexes containing Pd—C σ bonds, hydrides, olefins and acetylenes, dienes, π -allylic groups, cyclopentadienyls, and benzenes.
 - 70.2 Volume 2, Catalytic Reactions. An account of palladium-catalyzed reactions involving formation of C—C, C—O, C—H, C-halogen, C—N, C—S, or C—Si bonds, and heterogeneous reactions.

- "The Chemistry of Organometallic Compounds." Series editor, D. Seyferth. Wiley, New York.
- A26. M. Rosenblum, "Chemistry of the Iron Group Metallocenes: Ferrocene, Ruthenocene, Osmocene," volume 1, 1965.
- A71. H. Shapiro and F. W. Frey, "The Organic Compounds of Lead." 1968.
- A72. W. P. Neumann, "The Organic Chemistry of Tin." 1970. Translation and updating of "Die organische Chemie des Zinns." Ferdinand Enke Verlag, Stuttgart, 1967.
- A73. G. O. Doak and L. D. Freedman, "Organometallic Compounds of Arsenic, Antimony and Bismuth." 1970.
- A74. M. Lesbre, P. Mazerolles, and J. Satgé, "The Organic Compounds of Germanium." 1971.
- 74.1 Chapter 10, section 3: Organogermanium-transition metal complexes, pp. 672-688.

Compilations of Articles on Organometallic Themes

- A75. R. Ugo, ed., "Aspects of Homogeneous Catalysis." Carlo Manfredi, Milan. Volume 1 (1970) contains:
- 75.1 R. S. Coffey: Recent advances in homogeneous hydrogenation of carbon-carbon multiple bonds, pp. 5-76.
- 75.2 G. P. Chiusoli: Stereoselectivity in organic synthesis involving nickel-coordinated intermediates, pp. 77-107.
- 75.3 G. Lefebvre and Y. Chauvin: Dimerisation and codimerisation of olefinic compounds by coordination catalysis, pp. 108-203.
- 75.4 A. Andreetta, F. Conti, and G. F. Ferrari: Selective homogeneous hydrogenation of dienes and polyenes to monoenes, pp. 204-295.

The MTP International Review of Chemistry will appear in three series of eleven volumes each, together with three index volumes, surveying the period 1967-1971, concentrating on the last two years. Subsequent series will cover the periods 1971-1973, and 1974-1975. Each volume consists of a series of reviews by individual authors. At the time of writing these volumes had not appeared, and the exact topics covered will be detailed later.

- A76. MTP International Review of Science. Inorganic Chemistry Series One. Butterworths, London, and University Park, Baltimore, Maryland.

Other Books Containing Articles of Relevance to Organometallic Chemistry

- A77. C. Keller, "The Chemistry of the Transuranium Elements." Verlag Chemie, Weinheim, 1971. Chapter 8, Organometallic compounds of the actinides, pp. 187-193 (36). * Not as comprehensive as reference 4.39.
- A78. M. J. Udy, ed., "Chromium," ACS Monograph No. 132. Reinhold, New York, 1956. Volume 1: Chemistry of chromium and its compounds. Chapter 6, M. C. Udy: The physical and chemical properties of compounds of chromium. The last section, pp. 240-246, organometallic chromium compounds, is almost entirely concerned with a discussion of polyphenylchromium compounds, at the time of writing not recognized as bis- π -arenechromium derivatives.

• Figures in parentheses indicate number of references quoted in each article.

- A79. J. P. Snyder, ed.: "Nonbenzenoid Aromatics." Academic Press, New York. Volume 2 (1971) contains:
79.1 P. M. Maitlis and K. W. Eberius: Cyclobutadiene-metal complexes, pp. 359-409 (158).
- A80. I. Ugi, ed.: "Isonitrile Chemistry." Academic Press, New York, 1971. Contains:
80.1 A. Vogler: Coordinated isonitriles.
- A81. J. Falbe, "Synthesen mit Kohlenmonoxyd." Springer, Berlin, 1967. Surveys industrial syntheses based on carbon monoxide, including hydroformylation, carbonylation using metal carbonyl catalysts.
- A81a. English translation, "Carbon Monoxide in Organic Synthesis." Springer Publ., New York (1970).
- A82. W. Foerst: "New Methods of Preparative Organic Chemistry", Verlag Chemie, Weinheim/Academic Press, New York. Volume 6 (1971) contains:
82.1 J. Falbe: Cyclisation reactions with carbon monoxide, pp. 181-210 (102).
- A83. C. N. R. Rao and J. R. Ferraro, eds., "Spectroscopy in Inorganic Chemistry." Academic Press, New York, 1970. This book is mainly for inorganic chemists, but the following chapters mention some organometallic applications:
83.1 K. G. Das: Mass spectroscopy, pp. 173-208 (102).
83.2 A. Chakrovosty: High-resolution nuclear magnetic resonance, pp. 247-299 (136).
- A84. L. H. Jones, "Inorganic Vibrational Spectroscopy," volume 1. Dekker, New York, 1971. Chapter 5: Metal carbonyls, pp. 141-161 (38). Discussion of carbonyl stretching frequencies, force constants, etc., for binary carbonyls.
- A85. K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed. Wiley (Interscience), New York, 1970. Section III (Coordination Compounds) contains sections on:
III-7 Carbonyl, nitrosyl, and hydrido complexes, pp. 192-202.
III-8 Complexes of molecular nitrogen and other gases, pp. 202-205.
III-9 Complexes of phosphines and arsines, pp. 205-209 (174).
III-13 Complexes containing metal-metal bonds, pp. 219-220 (8).
III-24 Complexes of alkenes and alkynes, pp. 262-268.
III-25 Metal sandwich compounds, pp. 268-274 (78).
- A86. C. H. Bamford and C. F. H. Tipper, eds., "Comprehensive Chemical Kinetics." Elsevier, Amsterdam.
Volume 4 (1972), Decomposition of Inorganic and Organometallic Compounds, contains:
86.1 S. J. W. Price: Decomposition of metal alkyls, aryls, carbonyls and nitrosyls, pp. 197-257 (156); see especially section 2, homogeneous decomposition of metal carbonyls, and section 3.1, homogeneous decomposition of metal alkyls and aryls (of Cu, Ag, Au).
Volume 7 (1972), Reactions of Metallic Salts and Complexes and Organometallic Compounds, contains:
86.2 C. H. Langford and M. Parris: Reactions of Inert Complexes and Metal Organic Compounds, pp. 1-52 (170); see especially sections 6 and 7, complexes with B class ligands: the binary carbonyls, and the substituted carbonyls.

B. Reviews

A list of important review articles appearing up to the end of 1971 is published in the Appendix. During the year, the following volumes of

hardcover collections of reviews appeared; the references are included in the Appendix.

- B1. *Advances in Inorganic and Radiochemistry*, volume 13 (1971).
- B2. *Progress in Inorganic Chemistry*, ed. S. J. Lippard, volume 12 (1970), ed. J. O. Edwards, volume 13 (1970); ed. S. J. Lippard, volume 14 (1971).
- B3. *Advances in Organometallic Chemistry*, volume 10 (1972).
- A43. *Organometallic Reactions*, eds. E. J. Becker and M. Tsutsui, Wiley, New York. This continuing series was listed in the previous article in Section A, but the opportunity has now been taken to transfer any relevant articles to the Appendix.
- F5. *Preparative Inorganic Reactions*, volumes 6 and 7 (1971), ed. W. L. Jolly.

The review journal *Fortschritte der Chemische Forschung* has devoted two recent issues to organometallic topics. Volume 16, parts 3 and 4 surveys organometallic compounds in industry, and volume 25 is concerned with catalysis. Articles from these two compilations are listed in the Appendix.

C. Primary Journals

During the last year several new journals have appeared, in which papers of interest to organometallic chemists are published. Apart from the *Journal of Coordination Chemistry*, which deals with general aspects of the chemistry of complex compounds, vehicles for preliminary communication in the area of synthesis and structure determination have commenced. A detailed breakdown of these, and of the volumes of the Elsevier journals in organometallic chemistry are given.

- Journal of Organometallic Chemistry*, volumes 26–33 (1971).
- Organometallic Chemistry Reviews, Series A*, subject reviews volumes 6, 7 (1971).
- Organometallic Chemistry Reviews, Series B*, annual surveys, volumes 7, 8 (1971); 9, 10 (1972).
- Organometallics in Chemical Synthesis*, volume 1 (1970–1971).
- Journal of Coordination Chemistry*, volume 1 (1971). Gordon & Breach, New York, commenced publication, August 1971.
- Journal of Crystal and Molecular Structure*, volume 1 (1971), Plenum, New York.
- Synthetic Communications*, volume 1 (1971). Dekker, New York.
- Crystal Structure Communications*, volume 1 (1972). University of Parma.

D. Abstracting journals

There have been no further developments in this area, apart from the issue of the first indexes (to volume 71) of *Chemical Abstracts*, fully incorporating Registry Numbers.

E. Conferences

The 23rd IUPAC Conference in Boston, Massachusetts, during July 1971 contained a large section devoted to organometallic chemistry. The

plenary lectures delivered at this conference were published at the end of the year, with commendable speed, in six volumes. These consist of photographically reproduced typescripts, and in one case a manuscript, often also with hand-written alterations. The major lectures of interest in the present context are collected in Volume 6, containing lectures given at the Sessions "Organotransition metal chemistry" and "Homogeneous catalysis" although others were also given in sections dealing with organic synthesis.

E11. Special Lectures delivered at the 23rd International Congress on Pure and Applied Chemistry, Boston, Mass., July 1971. Six volumes, published by Butterworth, London, 1971.

Volume 2 contains:

- 11.1 J. Tsuji: Organic synthesis by means of transition metal complexes, pp. 107-119 (34).

Volume 4 contains:

- 11.2 P. S. Skell: Reactions of atoms: silicon and the high-boiling metals. Direct syntheses of organometallics, pp. 215-221 (10).

- 11.3 J. K. Kochi: Oxidation of alkyl radicals by metal complexes, pp. 337-404 (44).
Volume 6 contains:

- 11.4 R. Mason: The chemical bond in organotransition metal complexes: present status of experiment and theory, pp. 31-60 (44).

- 11.5 J. Lewis and R. S. Nyholm: Structure and reactions of metal complexes of chelate olefin ligands, pp. 61-99 (37).

- 11.6 A. W. Johnson: Transition metal complexes of macrocyclic ligands, pp. 101-132 (83).

- 11.7 D. Seyferth, J. E. Hallgren, R. J. Spohn, A. T. Wehrman, and G. H. Williams, The chemistry of alkylidene tricobalt nonacarbonyl and acetylenedicobalt hexacarbonyl complexes, pp. 133-149 (41).

- 11.8 C. G. Kreiter and E. O. Fischer: Transition metal carbene complexes: new spectroscopic and preparative results, pp. 151-168 (45).

- 11.9 G. P. Chiusoli: Catalysis of some insertion reactions by nickel complexes, pp. 169-199 (31).

- 11.10 A. Miyake, H. Kondo, M. Nishino, and S. Tokizane: Catalytic formation of macrocyclic polyenes from butadiene, pp. 201-211 (13).

- 11.11 D. G. H. Ballard: Polymerisation by homogeneous transition metal alkyl compounds, pp. 213-264 (25).

- 11.12 H. Bönnermann, C. Girard, W. Kopp, and G. Wilke: Homogeneous reactions catalysed by Group VIII metal systems, pp. 265-296 (25).

Proceedings of other international conferences which have been published include the 13th Coordination Chemistry Conference, and the 5th Organometallic Chemistry Conference.

E1.13 13 ICCS, Cracow-Zakopane, Sept. 1970. The plenary lectures are collected in *Pure Appl. Chem.* **27**, 1-164 (1971).

E2.5 5 ICOMC, Moscow, Aug. 1971. The plenary lectures are collected in *Pure Appl. Chem.* **30**, No. 3-4 (1972).

Some published proceedings of earlier conferences were omitted from the previous article, and relevant details are appended below:

- E12. Proceedings of the International Symposium on the Decomposition of Organometallics to Refractory Ceramics, Metals, and Metal Alloys, ed. K. S. Masdiyasi, University of Dayton Press, Dayton, Ohio, 1968.
- 12.1 R. B. King: π -Cyclopentadienylmolybdenum carbonyl derivatives, pp. 225–248.
- E13. Proceedings of the 3rd International Congress on Catalysis, ed. W. M. H. Sachter, G. C. A. Schmitt, and P. Zwietering, North-Holland Publ., Amsterdam, 1965. Two volumes. Contains:
- 13.1 R. S. Nyholm: Structure and reactivity of transition metal complexes. pp. 25–87 (79).
- 13.2 J. Halpern: Developments in homogeneous catalysis [using ruthenium complexes], pp. 146–162 (65).
- E14. Homogeneous catalysis with special reference to hydrogenation and oxidation. Proceedings of a conference, Liverpool, September, 1968, published as *Disc. Faraday Soc. No. 46*.
- E15. W. O. George, ed., "Spectroscopic Methods in Organometallic Chemistry." Butterworths, London, 1970. Proceedings of a conference, Kingston College of Technology, July, 1969. Previously listed as A42.
- 15.1 A. J. Downs: Vibrational spectroscopy, pp. 1–32 (58).
- 15.2 T. C. Gibb: Mössbauer spectroscopy, pp. 33–60 (22).
- 15.3 W. McFarlane: Nuclear magnetic Resonance, pp. 61–94 (51).
- 15.4 T. R. Spalding: Mass spectrometry, pp. 95–133 (86).
- 15.5 P. B. Ayscough: Electron spin resonance, pp. 134–177 (25).
- 15.6 P. G. Perkins: Electronic spectroscopy, pp. 178–193 (16).
- 15.7 Abstracts of 11 research papers, pp. 194–209.

Reports of conferences organized by the New York Academy of Sciences are published in the *Annals*, and several of these contain either original contributions or review articles concerned with aspects of organo-transition metal chemistry.

- E16. Annals of the New York Academy of Sciences. Since volume 100, contributions relevant to organo-transition metal chemistry have appeared in:
- 16.1 Vitamin B₁₂ coenzymes, *Ann. N.Y. Acad. Sci.* **112**, 547–921 (1964). I. Chemistry, chemical synthesis and biosynthesis of corrin coenzymes; II. Enzymic roles of cobinamide coenzymes; III. B₁₂-coenzymes in micro-organisms and animals.
- 16.2 Industrial synthesis and applications of organometallics, *Ann. N.Y. Acad. Sci.* **125**, 1–248 (1965).
- 16.3 Mass spectroscopy of organometallic compounds, *Ann. N.Y. Acad. Sci.* **136**, 95–122 (1966).
- 16.4 Purification of materials, *Ann. N.Y. Acad. Sci.* **137**, 1–402 (1966). Includes articles on organometallics as preparative intermediates.
- 16.5 Catalytic hydrogenation and analogous pressure reactions, *Ann. N.Y. Acad. Sci.* **145**, 1–206 (1967). Role of metal carbonyls, etc.

- 16.6 Prospectives of π -interactions in biological systems, *Ann. N.Y. Acad. Sci.* **153**, 1-388 (1969). Interesting speculations on the existence of π -complexes in biochemical reactions.
- 16.7 2nd Conference on catalytic hydrogenation and analogous pressure reactions, *Ann. N.Y. Acad. Sci.* **158**, 439-588 (1969). Hydrogenation via complex catalysts; cobalamin and cobaloxime chemistry.
- 16.8 Redistribution reactions in chemistry, *Ann. N.Y. Acad. Sci.* **159**, 1-334 (1969). Transition metal compounds feature in one paper only.
- 16.9 3rd Conference on catalytic hydrogenation and analogous pressure reactions, *Ann. N.Y. Acad. Sci.* **172**, 151-276 (1970). Catalysis by coordination complexes.
- 16.10 Homogeneous catalysis, *Ann. N.Y. Acad. Sci.* **172**, 479-569 (1971).

F. Synthesis

Last year saw the publication of an extremely useful book on synthetic techniques applicable to both inorganic and organometallic chemistry.

- F13. W. L. Jolly, "The Synthesis and Characterisation of Inorganic Compounds." Prentice-Hall, Englewood Cliffs, New Jersey, 1970. A very useful text, covering the principles of synthesis of inorganic compounds, many of which can be extrapolated to organometallics. Contains chapters on: synthetic principles, synthetic techniques, compound characterisation, synthesis.
- F1. "Inorganic Syntheses," vol. 13, ed. F. A. Cotton (1971).

G. Data Compilations

The formula index to Dub's Organometallic Compounds is now available.

- G1. M. Dub and R. W. Weiss, eds., "Organometallic Compounds." Springer, Berlin. Second edition, covering the literature 1937-1964. Vol. 1: Compounds of the transition metals (1966); vol. 2, Compounds of germanium, tin and lead (1967); vol. 3, Compounds of arsenic, antimony, and bismuth (1968); Formula index (1970).

In volumes supplementary to its main coverage of the chemistry of elements other than carbon, the Gmelin Institute has issued summaries of organo-vanadium and -chromium compounds in which the literature is covered to the end of 1970, and in some cases for chromium, to the end of January 1971. These volumes represent a departure from the usual policy of ignoring organic ligands followed by the Gmelin Institute, although the volume on Ruthenium (System No. 63) was the first to contain a treatment of organo-metallics in general for an element. The treatment is exhaustive, classified by ligand in terms of the number of carbon atoms attached to the metal.

- G6. "Gmelin's Handbuch der anorganischen Chemie," 8th ed., Gmelin-Institut Verlag Chemie, Weinheim.
6.1 Main Supplement, vol. 2: Vanadium-Organische Verbindungen; vol. 3: Chrom-Organische Verbindungen. Published together, 1971.
6.2 Ruthenium (system No. 63, Supplement volume), 1970.

All volumes published since 1957 have contained detailed indices, and numerous subheadings in English.

REFERENCE

1. M. I. Bruce, *Advan. Organometal. Chem.* **10**, 273 (1972).

APPENDIX*

As in the previous article, this Appendix collects and classifies some 100 review articles which have appeared to the end of 1971, together with some earlier ones which were omitted. The same classification scheme has been used, and the reference numbers follow. Two extra headings have been added:

44. Carbene complexes
45. Optical activity in organometallic complexes

* A separate author index to the Appendix can be found on p. 496.

Ref. No.	Authors	Reference	Title	No. of pages (No. of ref.)	Comments
1. Historical and biographical					
1.17	J. C. Bailar	<i>Pure Appl. Chem.</i> 27 , 1 (1971)	The development of transition metal chemistry in the United States of America	21 (150)	Plenary lecture, 13 ICCC; pp. 11–16, highlights organometallics, metal–metal bonds, complexes of N ₂ , O ₂
1.18	A. N. Nesmeyanov	<i>Advan. Organometal Chem.</i> 10 , 1 (1972)	My way in organometallic chemistry	78 (455)	Autobiographical
1.19	V. I. Spitsyn	<i>Pure Appl. Chem.</i> 27 , 193 (1971).	The development of coordination chemistry in the Soviet Union	33 (148)	Plenary lecture, 13 ICCC; pp. 214–217, organoelement compounds
2. Reviews of a general nature					
2.22	N. A. Belozerskii and O. D. Krichevskaya	<i>Probl. Sovrem. Khim. Koord. Soedin. No.</i> 3 , 246 (1970)	Practical use of carbonyl and other coordination compounds	8 (37)	Russ. Industrial applications
2.23	F. G. A. Stone	<i>Nature (London)</i> 232 , 534 (1971)	Perspectives in organometallic chemistry	6 (62)	Japan.
2.24	T. Yanagisawa, T. Endo, and T. Iwasaki	<i>Sekiyu To Sekiyu Kagaku</i> 14 (12), 98 (1970)	Ferrocene as a combustion additive; use as an antiknock and smoke reducing agent	6 (30)	
4. Organo-element chemistry					
4.39	R. G. Hayes and J. L. Thomas	<i>Organometal. Chem. Rev. Sect. A</i> 7 , 1 (1971)	Organometallic compounds of the lanthanides and actinides	50 (94)	Covers period 1964–1970
4.40	E. M. Larsen	<i>Advan. Inorg. Chem. Radiochem.</i> 13 , 1 (1970)	Zirconium and hafnium chemistry	133 (611)	Section III: compounds containing metal–carbon bonds

4.41	B. R. James	<i>Inorg. Chim. Acta Rev.</i> 4 , 73 (1970)	Homogeneous catalysis by ruthenium complexes	23 (300)	
4.42	J. Halpern	<i>Chem. Eng. News</i> , 44 (44), 68 (1966)	Coordination chemistry and homogeneous catalysis	8 (8)	Ruthenium complexes
4.43	R. F. Heck	<i>Fortschr. Chem. Forsch.</i> 16 , 221 (1971)	Addition-elimination reactions of palladium compounds with olefins	22 (40)	
4.44	I. Kuwajima	<i>Yuki Gosei Kagaku Kyokai Shi</i> 29 , 616 (1971)	Dialkylcopperlithium	4 (23)	Japan. Preparation and properties
4.45	C. Blomberg	<i>Chem. Tech. (Amsterdam)</i> 25 , 837 (1970)	Organosilver chemistry	2 (21)	
4.46	L. A. Paquette	<i>Accounts Chem. Res.</i> 4 , 280 (1971)	Catalysis of strained bond rearrangements by silver(I) ion	8 (43)	
4.37	B. Armer and H. Schmidbaur	<i>Angew. Chem.</i> 82 , 120 (1970); <i>Angew. Chem. Int. Ed. Engl.</i> 9 , 101 (1970); <i>Usp. Khim.</i> 40 , 1211 (1971)	The chemistry of organogold compounds	13 (94)	Russ. translation
4.47	B. F. G. Johnson	<i>Gold Bull.</i> 4 , 9 (1971)	The chemistry of gold	3	Recent advances in complex and organometallic chemistry
5. <i>Metal Carbonyls</i>					
5.13	J. G. Ameen and H. F. Durfee	<i>J. Chem. Educ.</i> 48 , 372 (1971)	The structure of metal carbonyls	4 (10)	
5.14	R. R. Ford	<i>Advan. Catal.</i> 21 , 51 (1970)	Carbon monoxide absorption on the transition metals	100 (212)	Surface adsorption
5.15	J. Grobe	<i>Chem. Unserer Zeit</i> 5 , 50 (1971)	Metal carbonyls	7 (4)	Structure, synthesis, catalytic applications
5.16	W. Hieber, R. Nast, and J. Sedlmeier	<i>Angew. Chem.</i> 64 , 465 (1952)	Results of recent research in the field of metal carbonyls	6 (46)	

(Continued)

Ref. No.	Authors	Reference	Title	No. of pages (No. of ref.)	Comments
7. Metal carbonyl anions					
7.4	R. B. King	<i>Trans. N.Y. Acad. Sci.</i> 28 , 889 (1966)	Metal carbonyl anions	6 (20)	
7.5	R. B. King	<i>Accounts Chem. Res.</i> 3 , 417 (1970)	Some applications of metal carbonyl anions in the synthesis of unusual organometallic compounds	11 (75)	
9. Metal carbonyl hydrides and halides					
9.10	J. Chatt	<i>Proc. Chem. Soc.</i> 318 (1962)	Hydrido- and related organo-complexes of transition metals	9 (16)	Chemical Society Tilden lecture
9.11	B. D. James	<i>Rec. Chem. Progr.</i> 31 , 199 (1970)	Recent developments in the inorganic chemistry of metal complex hydrides	11 (54)	
9.12	R. Colton	<i>Coord. Chem. Rev.</i> 6 , 269 (1971)	Steric effects in substituted halo-carbonyls of molybdenum and tungsten	16 (29)	Complexes with chelating bis-phosphines and -arsines
10. Complexes containing bonds between Transition Metals and Main Group Metals					
10.9	U. Belluco, G. Deganello, R. Pietropaolo, and P. Uguagliati	<i>Inorg. Chim. Acta Rev.</i> 4 , 7 (1970)	Complexes of platinum(II) with Group IV donor ligands	33 (149)	
10.10	E. H. Brooks and R. J. Cross	<i>Organometal. Chem. Rev. Sect. A</i> 6 , 227 (1970)	Group IVB metal derivatives of the transition metals	56 (209)	
10.11	C. H. van Dyke	<i>Prep. Inorg. React.</i> 6 , 157 (1971)	Inorganic derivatives of germane and digermane	76 (201)	Pp. 215–218: germyl-transition metal derivatives
10.12	C. H. Yoder and J. J. Zuckerman	<i>Prep. Inorg. React.</i> 6 , 81 (1971)	Heterocyclic compounds of the Group IV elements	75 (390)	Pp. 142–145: Group IV-transition metal bonds

11. Compounds containing bonds between transition metals (including cluster compounds)

- | | | | | | |
|-------|---|--|--|----------|--|
| 11.14 | F. A. Cotton | <i>Rev. Pure Appl. Chem.</i> 17 , 25 (1967) | Quadruple bonds and other multiple metal-to-metal bonds | 16 (26) | |
| 11.15 | F. A. Cotton | <i>Accounts Chem. Res.</i> 2 , 240 (1969) | Strong homonuclear metal-metal bonds | 8 (49) | |
| 11.16 | R. D. Johnston | <i>Advan. Inorg. Chem. Radiochem.</i> 13 , 471 (1970) | Transition metal clusters with π -acid ligands | 63 (386) | |
| 11.17 | K. Krogmann | <i>Angew. Chem.</i> 81 , 10 (1969); <i>Angew. Chem. Int. Ed. Engl.</i> 8 , 35 (1969) | Planar complexes containing metal-metal bonds | 8 (50) | |
| 11.18 | G. Palyi,
F. Piacenti, and
L. Marko | <i>Inorg. Chim. Acta Rev.</i> 4 , 109 (1970) | Methynyltricobalt enneacarbonyl compounds: preparation, structure and properties | 13 (94) | Last 10 years work on $\text{YCCo}_3(\text{CO})_9$; 39 complexes listed |

13. Lewis Base complexes—Group V donor atoms

- | | | | | | |
|-------|---------------|--|---|-----------|---|
| 13.6 | M. Kilner | <i>Advan. Organometal. Chem.</i> 10 , 115 (1972) | Nitrogen groups in metal carbonyls and related complexes | 84 (471) | |
| 13.7 | J. F. Nixon | <i>Advan. Inorg. Chem. Radiochem.</i> 13 , 363 (1970) | Recent progress in the chemistry of fluorophosphines | 110 (326) | Esp. pp. 410–439, 449–460: transition metal derivatives |
| 13.8 | S. Trofimenko | <i>Accounts Chem. Res.</i> 4 , 17 (1971) | Polypyrazolylborates, a new class of ligands | 6 (37) | |
| 13.9 | L. M. Venanzi | <i>Angew. Chem.</i> 76 , 689 (1964); <i>Angew. Chem. Int. Ed. Engl.</i> 3 , 453 (1964) | Complexes of tetradentate ligands containing phosphorus and arsenic | 8 (27) | |
| 13.10 | L. M. Venanzi | <i>Advan. Chem. Ser.</i> 98 , 66 (1971) | Hydrido complexes of platinum metals | 8 (45) | Containing polydentate ligands |

(Continued)

Ref. No.	Authors	Reference	Title	No. of pages (No. of ref.)	Comments
14. Lewis Base complexes—Group VI donor atoms					
14.8	R. Eisenberg	<i>Progr. Inorg. Chem.</i> 12 , 295 (1970)	Structural systematics of 1,1- and 1,2-dithiolato chelates	75 (173)	
14.9	E. Hoyer, W. Dietzsch, and W. Schroth	<i>Z. Chem.</i> 11 , 41 (1971)	Dithiolene chelates	13 (194)	
14.10	E. Uhlemann, H. Müller, and P. Thomas	<i>Z. Chem.</i> 11 , 401 (1971)	Synthesis, coordination chemistry and analytical uses of monothio- β -diketones	9 (90)	
14.11	G. Vitzhum and E. Lindner	<i>Angew. Chem.</i> 83 , 315 (1971); <i>Angew. Chem. Int. Ed. Engl.</i> 10 , 315 (1971)	Sulphinato complexes	12 (128)	
15. Metal-carbon σ-bonds					
15.22	G. B. Deacon	<i>Organometal. Chem. Rev. Sect. A</i> 5 , 355 (1970)	Syntheses of organometallic compounds by thermal decarboxylation.	18 (69)	
15.23	H. J. de Liefde Meijer and F. Jellinek	<i>Inorg. Chim. Acta</i> 4 , 651 (1970)	Alkyl, aryl and allyl complexes of some metallocenes	5 (43)	Derivatives of $(\pi\text{-C}_5\text{H}_5)_2\text{M}$ (M = Ti, Zr, V, Nb)
16. Fluorocarbon complexes					
16.13	C. Tamborski	<i>Trans. N.Y. Acad. Sci.</i> 28 , 601 (1966)	Perfluoro-organometallic compounds	10 (30)	
18. Hydrocarbon π-complexes—general reviews					
18.7	A. Z. Rubezhov and S. P. Gubin	<i>Advan. Organometal. Chem.</i> 10 , 347 (1972)	Ligand substitution in transition metal π -complexes	71 (290)	

19. *Hydrocarbon π -complexes—olefins and acetylenes*

- | | | | | | |
|-------|------------------------------------|---|---|-------------|--------------------------|
| 19.19 | G. Marr and
B. W. Rockett | <i>Educ. Chem.</i> 8 , 13
(1971) | Alkene and alkyne complexes of
transition metals | 4
(8) | |
| 19.20 | J. H. Nelson and
H. B. Jonassen | <i>Coord. Chem. Rev.</i>
6 , 27 (1971) | Mono-olefin and acetylene com-
plexes of nickel, palladium and
platinum | 37
(230) | |
| 19.21 | R. S. Nyholm | <i>Pure Appl. Chem.</i>
27 , 127 (1971) | Synthesis, structure and reactions
of chelate metal-olefin complexes | 18
(17) | Plenary lecture, 13 ICCC |

 22. *Hydrocarbon π -complexes—cyclopentadienyl and arene*

- | | | | | | |
|-------|----------------------------|--|--|------------|--|
| 22.14 | M. Hlevca and
I. Jitaru | <i>Rev. Fiz. Chim.,
Ser. A</i> 7 , 321 (1970) | Cyclopentadienyl metal compounds | 8
(15) | Rom. |
| 22.15 | P. M. Maitlis | <i>Trans. N.Y. Acad.
Sci.</i> 33 , 87 (1971) | Chemistry of some novel rhodium
and iridium complexes | 10
(19) | Pentamethylcyclopentadienyl
derivatives |
| 22.16 | M. Tsutsui | <i>Z. Chem.</i> 3 , 215
(1963) | The significance of Hein's π -
complexes. π -Radical hybridisa-
tion | 7
(33) | Bis-arene-chromiums |

 24. *Fluxional organometallic molecules*

- | | | | | | |
|------|---|--|--|-------------|--|
| 24.4 | K. Vrieze and
P. W. N. M.
van Leeuwen | <i>Progr. Inorg. Chem.</i>
14 , 1 (1971) | Studies of dynamic organometallic
compounds of the transition
metals by means of nuclear mag-
netic resonance | 63
(181) | |
|------|---|--|--|-------------|--|

 25. *Organic chemistry of metallocenes*

- | | | | | | |
|-------|---------------------------------|--|---|--------------|--|
| 25.43 | H. Imai | <i>Kagaku (Kyoto)</i> 25 ,
978 (1970) | Chemistry of ferrocenes. IV | 14
(33) | Japan. Acylated and halogenated
derivatives. See 25.8 |
| 25.44 | I. Motoyama and
M. Sato | <i>Yuki Gosei Kagaku
Kyokai Shi</i> 29 ,
664 (1971) | Recent developments in the chemi-
stry of metallocenes | 21
(227) | Japan. Progress after 1965 |
| 25.45 | E. W. Neuse and
H. Rosenberg | <i>J. Macromol. Sci.,
Rev. Macromol.
Chem.</i> 4 , 1 (1970) | Metallocene polymers | 145
(297) | |

(Continued)

Ref. No.	Authors	Reference	Title	No. of pages (No. of ref.)	Comments
25.46	C. U. Pittman	<i>Chem. Tech. (Washington)</i> 416 (1971)	Organic polymers containing transition metals	8 (35)	Ferrocene, cymantrene, etc.
25.47	D. W. Slocum and C. R. Ernst	<i>Organometal. Chem. Rev. Sect. A</i> 6, 337 (1970)	Metallocene homoannular electronic effects	17 (42)	
25.48	D. W. Slocum and C. R. Ernst	<i>Advan. Organometal. Chem.</i> 10, 79 (1972)	Electronic effects in metallocenes and certain related systems	36 (83)	
26. Metallocarborane complexes					
26.6	F. R. Scholer and L. J. Todd	<i>Prep. Inorg. React.</i> 7, 1 (1971)	Polyhedral boranes and heteroatom boranes	92 (237)	Esp. pp. 75–85: Polyhedral boranes containing a transition metal in the cage
27. Kinetics and mechanisms					
27.9	M. D. Johnson	<i>Rec. Chem. Progr.</i> 31, 143 (1970)	The mechanism of reaction of electrophiles with some σ -bonded organotransition ions	12 (25)	Plenary lecture, 13 ICCC
27.10	R. G. Pearson	<i>Accounts Chem. Res.</i> 4, 152 (1971)	Symmetry rules for chemical reactions	9 (20)	
27.11	R. G. Pearson	<i>Pure Appl. Chem.</i> 27, 145 (1971)	Orbital symmetry rules and the mechanism of inorganic reactions	16 (25)	
27.12	M. Tsutsui	<i>Ann. N.Y. Acad. Sci.</i> 93, 133 (1961)	π -Complex mechanism of catalysis: the aryl-coupling reaction	14 (16)	
28. Organic synthesis via organometallics					
28.36	B. F. G. Johnson	<i>Platinum Metals Rev.</i> 15, 60 (1971)	The platinum metals in organic synthesis	8	Organometallic complexes as preparative reagents

- | | | | | | |
|----------------------------------|---|--|--|-------------|--|
| 28.37 | C. Nieto de Castro,
M. J. Calhorda, and
V. M. Soares | <i>Tecnica (Lisbon)</i> 33
(403), 157 (1970) | Introduction to the study of transi-
tion metal complexes and their
use in organic synthesis | 9
(3) | Port. Reactions of ferrocene Job-
Cassal reaction |
| 28.38 | M. Ryang, J. Tsuji,
and K. Ohno | <i>Kagaku No Ryoiki,</i>
<i>Zokan</i> 89 , 93 (1970) | Carbonylation and related reactions | 46
(178) | Japan. |
| 28.39 | M. Ryang and
S. Tsutsumi | <i>Synthesis</i> 55 (1971) | Organic syntheses by means of
metal carbonyls | 15
(51) | |
| 28.40 | D. Seyferth and
R. J. Spohn | <i>Trans. N.Y. Acad.</i>
<i>Sci.</i> 33 , 625 (1971) | Organomercurial carbonylation. Use
of $\text{Co}_2(\text{CO})_8$ as a stoichiometric
and as a catalytic reagent | | |
| 28.41 | J. Tsuji | <i>Farumashia</i> 7 , 480
(1971) | Organic synthesis reactions using
palladium compounds | 4
(10) | Japan. |
| 28.42 | J. Tsuji and K. Ohno | <i>Synthesis</i> 157 (1969) | Decarbonylation reactions using
transition metal compounds | 9
(75) | |
| 29. Catalysis by organometallics | | | | | |
| 29.34 | J. C. Bailar | <i>Platinum Metals Rev.</i>
15 , 2 (1971) | The homogeneous hydrogenation of
soybean oil methyl ester | 7
(19) | Selectivity of Pd, Pt catalysts |
| 29.35 | G. C. Bailey | <i>Catal. Rev.</i> 3 , 37
(1969) | Olefin disproportionation | 24
(72) | |
| 29.36 | J. P. Candlin,
K. A. Taylor, and
D. T. Thompson | <i>Ind. Chim. Belge</i> 35 ,
1085 (1970) | Homogeneous catalysis in industry | 11
(14) | |
| 29.37 | R. Cramer | <i>Trans. N.Y. Acad.</i>
<i>Sci.</i> 33 , 97 (1971) | Rhodium(I)-catalysed isomerisa-
tion of linear butenes | 9
(13) | |
| 29.38 | Y. T. Eidus,
K. V. Puzitskii,
A. L. Lapidus, and
B. K. Nefedov | <i>Usp. Khim.</i> 40 , 806
(1971); <i>Russ.</i>
<i>Chem. Rev.</i> 40 ,
429 (1971) | Carbonylation of mono-olefinic and
mono-acetylenic hydrocarbons | 12
(237) | With Fe, Co, Ni, Rh, Pd complexes |
| 29.39 | J. L. Garnett | <i>Catal. Rev.</i> 5 , 229
(1971) | π -Complex intermediates in homo-
geneous and heterogeneous cata-
lytic exchange reactions of hydro-
carbons and derivatives with
metals | 39
(78) | |

(Continued)

Ref. No.	Authors	Reference	Title	No. of pages (No. of ref.)	Comments
29.40	J. Hanzlik	<i>Chem. Listy</i> 65 , 454 (1971)	The system of cobalt cyanide complexes and its position in homogeneous catalysis	32 (144)	Czech.
29.41	G. Henrici-Olivé and S. Olivé	<i>Angew. Chem.</i> 83 , 121 (1971); <i>Angew. Chem. Int. Ed. Engl.</i> 10 , 105 (1971)	Influence of ligands on the activity and specificity of soluble transition metal catalysts	11 (60)	
29.42	P. M. Henry	<i>Trans. N.Y. Acad. Sci.</i> 33 , 41 (1971)	Mechanisms of palladium(II)-catalyzed reactions	24 (67)	Wacker reaction; $\pi \rightarrow \sigma$ rearrangement
29.43	K. L. Khidekel', A. D. Shebaldova, and I. V. Kalechits	<i>Usp. Khim.</i> 40 , 1416 (1971); <i>Russ. Chem. Rev.</i> 40 , 669 (1971)	Catalytic disproportionation of unsaturated hydrocarbons	10 (94)	
29.44	J. E. Lyons, L. E. Renwick, and J. L. Burmeister	<i>Ind. Eng. Chem., Prod. Res. Develop.</i> 9 , 2 (1970)	Use of transition metal catalysts as selective hydrogenation catalysts	19 (121)	
30. Organometallic polymerisation catalysts					
30.18	C. H. Bamford	<i>J. Appl. Chem.</i> 13 , 525 (1963)	Recent advances in polymer science	13 (77)	Organometallic initiators
30.19	J. Boor	<i>Ind. Eng. Chem., Prod. Res. Develop.</i> 9 , 437 (1970)	Review of recent literature on Ziegler-type catalysts	32 (128)	
30.20	W. Cooper	<i>Ind. Eng. Chem., Prod. Res. Develop.</i> 9 , 457 (1970)	Aspects of mechanism of coordination polymerisation of conjugated dienes	10 (74)	
30.21	F. Dawans and P. Teyssié	<i>Ind. Eng. Chem., Prod. Res. Develop.</i> 10 , 261 (1971)	π -Allyl-type polymerisation	9 (51)	

30.22	J. Furukawa	<i>Pure Appl. Chem.</i> 26 , 153 (1971)	Copolymerisation of vinyl chloride by organometallic compounds	19 (8)	Main lecture, 7th Micro-symposium on Macromolecules, Prague, Sept. 1970. Ziegler-type catalysts
30.23	A. Gumboldt	<i>Fortschr. Chem. Forsch.</i> 16 , 299 (1971)	Organometallic compounds as catalysts of olefin polymerisation	30 (70)	
30.24	G. Henrici-Olivé and S. Olivé	<i>Fortschr. Hochpolym. Forsch.</i> 6 , 421 (1969)	Coordinative polymerisation with soluble transition metal catalysts	52 (72)	
30.25	G. Henrici-Olivé and S. Olivé	<i>Angew. Chem.</i> 83 , 782 (1971); <i>Angew. Chem. Int. Ed. Engl.</i> 10 , 776 (1971)	Vanadium and chromium catalysts for polymerisation of ethylene	11 (49)	
30.26	V. P. Mardykin, A. M. Antipova, and P. N. Gaponik	<i>Usp. Khim.</i> 40 , 24 (1971); <i>Russ. Chem. Rev.</i> 40 , 13 (1971)	Three-component complex organometallic catalysts for polymerisation of olefinic hydrocarbons	11 (236)	
30.27	Y. Uchida and M. Hidai	<i>Kagaku No Ryoiki, Zokan</i> 89 , 139 (1970)	Oligomerisation by using transition metal catalysts	18 (61)	Japan.
30.28	H. Weber	<i>Fortschr. Chem. Forsch.</i> 16 , 329 (1971)	Organometallic compounds as catalysts for the preparation of stereopolymers	35 (138)	
30.29	A. Yamamoto	<i>Kobunshi</i> 19 , 765 (1970)	Polymerisation by transition metal alkyl and hydride complexes	10 (43)	Japan.
31. <i>Oxidative-addition and related reactions</i>					
31.16	E. Bayer and P. Schretzmann	<i>Struct. Bonding (Berlin)</i> 2 , 181 (1967)	Reversible oxygenation of metal complexes	70 (247)	Mainly Co, Fe-haem, but includes Vaska adducts

(Continued)

Ref. No.	Authors	Reference	Title	No. of pages (No. of ref.)	Comments
31.17	A. P. Ginsberg, W. E. Lindsell, and W. E. Silverthorn	<i>Trans. N.Y. Acad. Sci.</i> 33 , 303 (1971)	Reactions of carbon subsulphide and of elementary phosphorus, sulphur and selenium with complexes of the platinum metals	10 (29)	
31.18	A. Wojcicki	<i>Accounts Chem. Res.</i> 4 , 344 (1971)	Sulphur dioxide insertion reactions of transition metal alkyls and related complexes	9 (85)	
<i>33. Photochemistry</i>					
33.4	R. E. Bozak	<i>Advan. Photochem.</i> 8 , 227 (1971)	Photochemistry in the metallocenes	18 (57)	
33.5	I. Moritani and T. Hosokawa	<i>Kagaku No Ryoiki, Zokan</i> 93 , 183 (1970)	Photoreactions in organometallic compounds	29 (81)	
33.6	J. H. Richards and N. Pisker-Trifunac	<i>J. Paint Technol.</i> 41 , 363 (1969)	Metallocene photochemistry	9 (29)	
<i>34. Organometallic complexes of biological interest</i>					
34.6	A. Bigotto, G. Costa, G. Mestroni, G. Pellizer, A. Puxeddu, E. Reisenhofer, L. Stefani, and G. Tauzher	<i>Inorg. Chim. Acta Rev.</i> 4 , 41 (1970)	Extension of the "model" approach to the study of coordination chemistry of vitamin B ₁₂ group compounds	9 (49)	
<i>36. Physical methods—infrared spectroscopy</i>					
36.8	S. F. A. Kettle and I. Paul	<i>Advan. Organometal. Chem.</i> 10 , 199 (1972)	Infrared intensities of metal carbonyl stretching vibrations	38 (138)	

36.9	E. Maslowsky	<i>Chem. Rev.</i> 71 , 507 (1971)	Vibrational spectra of intra- and inter-metal and semi-metal bonds	18 (248)	
38. <i>Physical methods—mass spectrometry</i>					
38.5	R. B. King	<i>Fortschr. Chem. Forsch.</i> 14 , 92 (1970)	The fragmentation of transition metal organometallic compounds in the mass spectrometer	35 (81)	
40. <i>Structural studies</i>					
40.10	M. R. Churchill	<i>Perspect. Struct. Chem.</i> 3 , 91 (1970)	Structural studies on transition metal complexes containing σ - bonded carbon atoms	74 (242)	
40.11	J. D. Dunitz	<i>Perspect. Struct. Chem.</i> 2 , 1 (1968)	Conformations of medium rings	70 (176)	Often studied as Ag^+ adducts
42. <i>Molecular nitrogen (dinitrogen) complexes</i>					
42.20	J. Chatt	<i>Pure Appl. Chem.</i> 24 , 425 (1970)	Molecular nitrogen as a ligand	17 (67)	Plenary lecture, 12 ICCC
42.21	R. H. Fischer and P. B. Venuto	<i>Bull. N.J. Acad. Sci.</i> 15 (1-2), 1 (1970)	Metal complexes as inorganic nitro- gen-fixing systems	9 (77)	
42.22	M. Ichikawa	<i>Kagaku No Ryoiki</i> 24 , 863 (1970)	Fixation of molecular nitrogen and ammonia synthesis	18 (76)	Japan.
42.23	G. J. Leigh	<i>Prep. Inorg. React.</i> 7 , 165 (1971)	Complexes of dinitrogen	19 (86)	
42.24	J. R. Postgate	<i>Chem. Tech. (Amsterdam)</i> 25 , 627 (1970)	Nitrogen binding	3	Newer methods to examine N- fixation by micro-organisms
42.25	G. N. Schrauzer	<i>Advan. Chem. Ser.</i> 100 , 1 (1971)	Model studies in nitrogen fixation and cobalamin chemistry	20 (12)	
42.26	W. D. P. Stewart	<i>Science</i> 158 , 1426 (1967)	Nitrogen-fixing plants	7 (59)	
42.27	Y. Uchida	<i>Kagaku To Seibutsu</i> 8 , 202 (1970)	Nitrogen fixation	9 (29)	By transition metal complexes

(Continued)

Ref. No.	Authors	Reference	Title	No. of pages (No. of ref.)	Comments
43. Other topics of related interest					
43.8	W. Beck	<i>Organometal Chem. Rev. Sect. A</i> 7, 159 (1971)	Complex metal fulminates	32 (118)	
44. Carbene complexes					
44.1	E. O. Fischer	<i>Pure Appl. Chem.</i> 24, 407 (1970)	Structure, bonding and reactivity of (stable) transition metal carbonyl carbene complexes	17 (35)	Plenary lecture, 12 ICC
45. Optical activity in organometallic complexes					
45.1	H. Brunner	<i>Angew. Chem.</i> 83, 274 (1971); <i>Angew. Chem. Int. Ed. Engl.</i> 10, 249 (1971)	Optical activity from asymmetric transition metal atoms	12 (88)	
45.2	G. Paiaro	<i>Organometal. Chem. Rev. Sect. A</i> 6, 319 (1970)	Optical activity in olefin-metal complexes	17 (67)	

Author Index¹

Reviews of Organo-Transition Metal Chemistry 1971

A

Ameen, J. G., 5.13
Antipova, A. M., 30.26

B

Bailar, J. C., 1.17, 29.34
Bailey, G. C., 29.35
Bamford, C. H., 30.18
Bayer, E., 31.16
Beck, W., 43.8
Belluco, U., 10.9
Belozerskii, N. A., 2.22
Bigotto, A., 34.6
Blomberg, C., 4.46
Boor, J., 30.19
Bozak, R. E., 33.4
Brooks, E. H., 10.10
Brunner, H., 45.1
Burmeister, J. L., 29.44

C

Calhorda, M. J., 28.37
Candlin, J. P., 29.36
Chatt, J., 9.10, 42.20
Churchill, M. R., 40.10
Colton, R., 9.12
Cooper, W., 30.20
Costa, G., 34.6
Cotton, F. A., 11.14, 11.15
Cramer, R., 29.37
Cross, R. J., 10.10

D

Dawans, F., 30.21
Deacon, G. B., 15.22
Deganello, G., 10.9
de Liefde Meijer, H. J., 15.23

Dietzsche, W., 14.9
Dunitz, J. D., 40.11
Durfee, H. F., 5.13

E

Eidus, Y. T., 29.38
Eisenberg, R., 14.8
Endo, T., 2.24
Ernst, C. R., 25.47, 25.48

F

Fischer, E. O., 44.1
Fischer, R. H., 42.21
Ford, R. R., 5.14
Furukawa, J., 30.22

G

Gaponik, P. N., 30.26
Garnett, J. L., 29.39
Ginsberg, A. P., 31.17
Grobe, J., 5.15
Gubin, S. P., 18.7
Gumboldt, A., 30.23

H

Halpern, J., 4.42
Hanzlik, J., 29.40
Hayes, R. G., 4.39
Heck, R. F., 4.43
Henrici-Olivé, G., 29.41, 30.24, 30.25
Henry, P. M., 29.42
Hidai, M., 30.27
Hieber, W., 5.16
Hlevca, M., 22.14
Hosokawa, T., 33.5
Hoyer, E., 14.9

¹ Author Index for appendix (pp. 455–468) to the article “The Literature of Organo-Transition Metal Chemistry 1971” by M. I. Bruce.

I

Ichikawa, M., 42.22
 Imai, H., 25.43
 Iwasaki, T., 2.24

J

James, B. D., 9.11
 James, B. R., 4.41
 Jellinek, F., 15.23
 Jitaru, I., 22.14
 Johnson, B. F. G., 4.44, 4.48, 28.36
 Johnson, M. D., 27.9
 Johnston, R. D., 11.16
 Jonassen, H. B., 19.20

K

Kalechits, I. V., 29.43
 Kettle, S. F. A., 36.8
 Khidekel', K. L., 29.43
 Kilner, M., 13.6
 King, R. B., 7.4, 7.5, 38.5
 Krichevskaya, O. D., 2.22
 Krogmann, K., 11.17
 Kuwajima, I., 4.45

L

Lapidus, A. L., 29.38
 Larsen, E. M., 4.40
 Leigh, G. J., 42.23
 Lindsell, W. E., 31.17
 Lindner, E., 14.11
 Lyons, J. E., 29.44

M

Maitlis, P. M., 22.15
 Mardykin, V. P., 30.26
 Markó, L., 11.18
 Marr, G., 19.19
 Maslowsky, E., 36.9
 Mestroni, G., 34.6
 Moritani, I., 33.5
 Motoyama, I., 25.44
 Müller, H., 14.10

N

Nast, R., 5.16
 Nefedov, B. K., 29.38
 Nelson, J. H., 19.20
 Nesmeyanov, A. N., 1.18
 Neuse, E. W., 25.45
 Nieto de Castro, C., 28.37
 Nixon, J. F., 13.7
 Nyholm, R. S., 19.21

O

Ohno, K., 28.38, 28.42
 Olivé, S., 29.41, 30.24, 30.25

P

Paiano, G., 45.2
 Palyi, G., 11.18
 Paquette, L. A., 4.47
 Paul, I., 36.8
 Pearson, R. G., 27.10, 27.11
 Pellizer, G., 34.6
 Piacenti, F., 11.18
 Pietropaolo, R., 10.9
 Pisker-Trifunac, N., 33.6
 Pittman, C. U., 25.46
 Postgate, J. R., 42.24
 Puxeddu, A., 34.6
 Puzitskii, K. V., 29.38

R

Reisenhofer, E., 34.6
 Renwick, L. E., 29.44
 Richards, J. H., 33.6
 Rockett, B. W., 19.19
 Rosenberg, H., 25.45
 Rubezhov, A. Z., 18.7
 Ryang, M., 28.38, 28.39

S

Sato, M., 25.44
 Scholer, F. R., 26.6
 Schrauzer, G. N., 42.25
 Schretzmann, P., 31.16
 Schroth, W., 14.9

Sedlmeier, J., 5.16
 Seyferth, D., 28.40
 Shebaldova, A. D., 29.43
 Silverthorn, W. E., 31.17
 Slocum, D. W., 25.47, 25.48
 Soares, V. M., 28.37
 Spitsyn, V. I., 1.19
 Spohn, R. J., 28.40
 Stefani, L., 34.6
 Stewart, W. D. P., 42.26
 Stone, F. G. A., 2.23

T

Tamborski, C., 16.13
 Tauzher, G., 34.6
 Taylor, K. A., 29.36
 Teyssié, P., 30.21
 Thomas, J. L., 4.39
 Thomas, P., 14.10
 Thompson, D. T., 29.36
 Todd, L. J., 26.6
 Trofimenko, S., 13.8
 Tsuji, J., 28.38, 28.41, 28.42
 Tsutsui, M., 22.16, 27.12
 Tsutsumi, S., 28.39

U

Uchida, Y., 30.27, 42.27
 Uguagliati, P., 10.9
 Uhlemann, E., 14.10

V

van Dyke, C. H., 10.11
 van Leeuwen, P. W. N. M., 24.4
 Venanzi, L. M., 13.9, 13.10
 Venuto, P. B., 42.21
 Vitzhum, G., 14.11
 Vrieze, K., 24.4

W

Weber, H., 30.28
 Wojcicki, A., 31.18

Y

Yamamoto, A., 30.29
 Yanagisawa, T., 2.24
 Yoder, C. H., 10.12

Z

Zuckerman, J. J., 10.12

Author Index

Numbers in parentheses are reference numbers and indicate that an author's work is referred to although his name is not cited in the text. Numbers in italics show the page on which the complete reference is listed.

A

Abbott, Jr., R. K., 147, 162, 203
 Abel, E. W., 254(1), 283(1), 300(1), 323
 Abeles, R. H., 410, 415(7), 441
 Ablov, A. V., 63(2), 74(1, 2), 81
 Abouaf, R., 212(1), 249
 Adams, D. M., 286(2), 323
 Adams, R. D., 283(3), 291(3), 323
 Adin, A., 367(1), 369(1), 371(1), 397(1), 422, 441
 Adloff, J. P., 222, 234, 247(33), 249, 250
 Adloff, M., 234(2), 249
 Agnes, G., 389(2), 424(2), 427(2, 3), 441
 Ahrland, S., 161(1), 202
 Akerman, K., 218, 222, 246, 251
 Alexander, J. J., 111(1, 2, 2a), 116(2), 121(1), 126(1, 2), 139
 Allen, L. E., 117(236), 134(236), 145
 Almasy, G., 131(167), 143
 Alper, H., 61(2a), 81
 Altland, H. W., 158(2, 147, 149), 159(147), 169(147), 172(147), 192(148), 202, 205
 Amberger, E., 256(4), 264(4), 283(4), 291(4), 323
 Anderson, C. B., 177(3), 181(3), 202
 Anderson, R. L., 123(59), 141
 Andrianov, K. A., 310(4a), 323
 Anet, F. A. L., 181, 202
 Ang, H. G., 254(242), 330
 Angelici, R. J., 45(3), 47, 53, 61(3), 81, 100(3), 101(3), 109(3), 139
 Anisimov, K. N., 91(6), 122(178, 179, 180, 181, 182, 184), 124(4), 125(4, 184), 126(181, 182, 183, 184), 139, 144, 153(108, 109), 204, 256(193, 194), 286(154, 193), 327, 328
 Antonova, A. B., 286(154), 327
 Antus, S., 190(118), 205
 Araneo, A., 68(6), 81

Arase, A., 15(63), 20
 Archer, N. J., 258(5), 289(5), 291(5), 299(5), 307(5), 323
 Arora, S. K., 11(33), 19
 Ash, M. J., 257(6), 272(6), 273(6), 276(6), 283(6), 323
 Ashley-Smith, J., 137(5), 139
 Aslanov, L., 282(6a), 323
 Astakhova, I. S., 91(6), 139
 Astrakhanov, M. I., 299(204), 301(204), 329
 Ataka, K., 75(111), 84
 Aumann, R., 52, 81
 Aylett, B. J., 254(7), 255(10), 256(12), 257(9), 264(10, 12), 265(10), 270(8, 9, 10), 272(9, 10), 274(11, 12), 275(9, 10, 11, 12), 276(9), 278(10), 279(10, 11, 12), 280(12), 281(205), 283(8), 285(9, 10), 286(12, 205), 287(9, 10), 323, 329

B

Baay, Y. L., 257(13, 14), 258(13, 14), 274(13, 14), 278(13), 299(13, 14), 306(13, 14), 307(13, 14), 323
 Badley, E. M., 42, 43(10), 45, 46(8, 9), 80(8, 9), 81
 Bailey, N. A., 136(7), 139, 344(4), 349(4), 361(4), 378(4), 381(4), 391(4), 441
 Bailey, R. A., 57(95), 64(94), 84
 Bainbridge, A., 92(8), 139
 Baird, M. C., 134(9, 10, 11), 135(10), 139(12), 139, 254(16), 259(15), 260(15), 285(15), 323, 360(5), 383(5), 396(5), 441
 Balch, A. L., 36(11), 43(33), 44(33), 45(99), 46(99), 61(99), 65(11), 66(11), 67(11), 68(11), 74(33), 80(33), 81, 82, 84
 Bald, J. F., 280(17), 323
 Balk, H.-J., 260(215), 262(215), 268(215), 293(215), 329

- Ball, R., 262(18), 290(18), 323
 Ballard, D. G. H., 316(19), 322(19), 323(19), 323
 Bamford, C. H., 51, 81
 Bamford, W. R., 308(20), 324
 Bancroft, G. M., 59(13, 14, 15, 16, 17), 81, 82, 289(21), 324
 Bandyopadhyay, P., 57(134), 85
 Banks, R. G., 350(6), 351(6), 434(6), 441
 Bannister, W. D., 123(13, 15), 124(13, 15), 125(14, 16), 139, 140
 Barbieri, R., 164(32), 202
 Barnett, K. W., 93(227), 109(19a), 118(19b), 119(17, 18, 20), 120(17, 20), 121(17, 18, 19a, 20), 128(17), 129(227), 137(19), 140, 145, 330
 Barnett, R., 410, 415(7), 441
 Bartell, L. S., 150, 205
 Bartholomew, G. A., 209(3), 210, 249
 Bartlett, E. H., 383(9), 423, 434(8), 425(9), 441
 Baryshnikov, L. I., 153(109), 204
 Basolo, F., 55(69), 56(69), 69(98), 83, 84, 94(48, 168), 97(48), 98(168), 99, 100(48, 214), 104(48, 168), 107(169), 109(169), 114(169), 120(48), 123(170), 125(168), 127(48), 140, 143, 145
 Basters, J., 358(10), 434(10), 436(10), 438(10), 441
 Batyr, D. G., 63(1, 2), 74(1, 2), 81
 Baulch, D., 234(21), 250
 Baumgartner, F., 81(57), 83, 224, 225(14), 228, 229, 232, 236(5, 6, 7, 8, 9), 237(9, 10, 11, 13), 241(15), 245(4, 9, 11, 12, 13), 249, 250
 Bayston, J. H., 350(11), 441
 Beach, D. L., 118(19b), 140
 Beale, R. N., 350(11), 441
 Beck, K. R., 308(22), 324
 Beck, W., 41, 80, 82, 122(22), 125(127), 133(126), 140, 142
 Beckham, T. M., 356, 369(160), 371(159), 400, 407(159), 410, 413(159), 415(159), 416(159), 420(159), 421(159), 422(160), 423(160), 438(159), 445
 Bednarski, T. M., 173(71), 186, 203
 Beletskaya, I. P., 158(134), 205
 Belluco, U., 46(48), 82, 95(233), 135(87, 233), 138(57a), 141, 145, 254(242), 330
 Benaim, J., 120(23), 128(23), 140
 Bendle, S., 389(2), 424(2), 427(2), 441
 Benedict, J. J., 37(146), 38(20, 146), 39(146), 40, 42(20), 44(146), 51(148), 57(20, 146, 148), 61(146, 148), 82, 85, 124(225), 145
 Benkeser, R. A., 298(23, 25), 299(25), 301(23), 308(22), 324
 Bennett, C. R., 128(151), 143, 256(164), 263(164), 288(164), 312(164), 319(164), 321(164), 327
 Bennett, E. W., 310(25a), 324
 Bennett, M. A., 125(24, 25), 140, 258(25b), 259(25b), 324
 Bennett, M. J., 261(26, 26a), 262(18), 290(18), 291(26, 26a), 323, 324
 Bentham, J. E., 259(27), 260(27), 266(27), 268(27), 270(27), 271(27), 274(27), 277(27), 286(27), 302(27, 29), 303(27, 28), 324
 Berger, M. N., 90(26), 140
 Bergerud, J. R., 268(140a), 327
 Bergmann, E. D., 134(34), 140
 Berndt, A. F., 244(16), 250
 Bernhauer, K., 360, 386(176), 425(13), 441, 446
 Berrett, R. R., 59(21), 82
 Berry, A., 92(27), 140
 Berry, A. D., 255(31), 264(31), 265(31), 266(31), 272(31), 273(31), 289(30), 324
 Bethea, III, T. W., 172(70), 174(70), 177(70), 203
 Bibler, J. P., 91(28), 93(28), 100(28), 127(28), 128(28), 140, 324
 Bichler, R. E. J., 278(34), 279(33), 324
 Bied-Charreton, C., 388(15), 414(15), 441
 Bieniek, D., 433(12), 438(12), 441
 Bigley, D. B., 11(33), 19
 Bigorgne, M., 115(200), 130(200), 144, 256(156), 257(155, 156), 258(155, 156), 266(156), 272(156), 285(157), 288(156), 327
 Bigotto, A., 345(16), 346(16), 347(16), 354(16), 356(16), 361(16), 366(16), 372(16), 378(16), 379(16), 380(16), 388(16), 391(16), 441
 Bilevitch, K. A., 149(120), 155(120), 205
 Birch, S. F., 155(6), 195(6), 202

- Bird, C. W., 90(31), 112(29), 118(30), 140
 Bisnette, M. B., 111(141), 119(144), 121(141), 124(143, 144), 126(141), 128(142, 143, 144), 143
 Biswas, D. K., 402(135), 445
 Bittler, K., 118(32), 138(32), 140
 Bjorklund, C., 53(157), 85
 Bjerkelund, K., 239(17), 250
 Blackmore, T., 126(33), 140, 256(35), 257(35), 288(35), 324
 Blake, D. M., 105(160), 109(160), 110(160), 136(159, 160), 137(159), 143
 Blum, J., 134(34), 137(33a), 140
 Bock, R., 149(7), 202
 Bogdanovic, B., 334(178), 336(178), 446
 Bolton, E. S., 51(22), 82
 Bonati, F., 21, 22(90), 26, 39(100), 41(90), 43(90), 45(100), 46(25, 27), 49, 50(23), 52(90), 54, 58, 64(90), 65(90), 66(90), 68(6), 70(90), 74(25), 75(25), 76(27, 90), 79(27, 90), 80(25, 100), 81(100), 81, 82, 83, 84
 Boocock, G., 90(26), 140
 Boorman, P. M., 65(28), 82
 Booth, B. L., 92(35), 94(37), 103(37), 105(37), 107(37), 108(37), 123(13), 124(13, 35), 125(14, 36, 37), 139, 140
 Booth, G., 92(39), 137(38, 39), 138(38, 39), 139(39), 140, 336(17), 345(17), 378(17), 380(17), 442
 Booth, J., 133(40), 140
 Booth, M. R., 279(33), 324
 Bor, G., 101(177), 112(177), 131(167), 132(177), 143, 144
 Borak, J., 234(65), 251
 Borod'ko, Y. G., 353(142), 368(142), 369(142), 371(142), 372(142), 445
 Borodulina-Shvets, V. I., 373(18), 374(18), 442
 Boronina, N. N., 370(175), 424(175), 446
 Boschetto, D. J., 117(237), 128(237), 145
 Boschi, T., 34(49), 35, 39(46, 49), 44(46), 46(25, 48), 66(29), 74(25, 29, 30, 49), 75(25, 47), 80(25), 82
 Bott, R. W., 192(8), 202, 298(105), 299(105), 300(105), 302(105), 326
 Bowden, K., 152(9), 164(9), 202
 Brainina, E. M., 151(113), 153(113), 154(113), 204
 Braterman, P. S., 318(35a, 244), 324, 330
 Brauman, J. I., 130(70a), 141
 Braun, G., 125(127), 131(131), 142, 342(81), 443
 Breckenridge, J. H., 289(36), 324
 Breil, H., 36(31), 74(31), 82
 Breslow, D. S., 131(41, 120, 121, 122, 123), 140, 142, 272(137), 283(138), 307(138), 327
 Bressan, M., 268(37), 324
 Breuer, E., 15(55), 20
 Brier, P. N., 285(38), 324
 Brinckmann, F. E., 155(132), 205
 Brittain, J. N., 289(235), 330
 Brodie, J. D., 348(20), 384(20), 417(19), 421(19), 442
 Brookes, A., 257(6), 262(39), 272(6), 273(6), 276(6), 283(6), 292(39), 323, 324
 Brooks, E. H., 254(40), 262(18), 290(18), 292(40), 323, 324
 Brown, C. K., 133(241, 242), 134(43, 242), 136(42, 242), 140, 145
 Brown, D. M., 174(10), 202
 Brown, H. C., 3(3), 5(7), 6(8), 8(10, 11, 12, 13, 14, 15, 16, 17), 9(12, 18, 19, 20, 21, 22), 10(23, 24, 25, 26), 11(27, 28, 29, 30, 31, 32, 33, 34), 12(28, 35, 36), 13(35, 37, 38, 39, 40, 41, 42, 45), 14(35, 43, 44, 45, 46, 47, 48, 49), 15(35, 50, 51, 52, 53, 63), 16(58, 60, 64, 65, 66), 18(67), 19, 20, 163, 178(11, 12), 202
 Brown, T. L., 63, 83, 91(125), 92(27), 133(125), 140, 142, 258(196a), 289(41, 196a), 324, 328, 346(116a), 367(80, 116a), 368(80, 116a), 429(80), 443, 444
 Bruce, M. I., 122(44), 125(133), 126(33, 44), 140, 142, 150(14) 202, 256(35), 257(35, 43), 275(43), 287(42), 288(35), 324
 Brückner, S., 344(21, 22, 23, 24), 347(21, 24), 348(23), 442
 Brunner, H., 57, 82, 128(45, 46), 140
 Buchanan, D. H., 353(95), 370(95), 371(95), 372(95), 388(95), 444
 Bufe, U. E., 81(97), 83
 Bunnell, C. A., 108(60), 122(60), 141
 Burg, A. B., 3(2, 3), 4(4, 5), 5, 18

Burger, K., 41(19), 80(19), 82
 Burke, A., 43(33), 44(33), 74(33), 80(33), 82
 Burmeister, J. L., 268(44), 324
 Burnett, M. G., 435(24a), 442
 Burrows, M. L., 298(23), 300(23), 324
 Burt, R., 118(47), 140
 Busch, D. H., 346(131), 350(131), 351(60), 365(60, 130, 131), 376(131), 387(25, 60, 130), 388(130, 131), 405(131), 406(131), 414(131), 432(60), 442, 443, 445
 Buschetto, D. J., 431(177), 446
 Butler, I. S., 94(48), 97(48), 100, 104(48), 119(48), 120(48), 127(48), 140
 Butler, W. M., 43(34), 74(34), 80(34), 82
 Byrd, J. E., 188(15), 202

C

Calderazzo, F., 89(191), 94(49, 50, 51, 52, 54), 101(54), 105(50, 51), 107(50, 51, 54), 108(50, 51, 192), 109, 112(191), 113(191, 192), 114, 122(50, 51, 55, 193), 116, 122(54), 123(52, 53, 54), 124(51), 125(50, 51, 52, 191, 192), 141, 144, 268(45), 272(45), 324, 342(64), 345(64), 377(26, 64), 378(64), 386(26, 64), 390(64), 392(64), 425(64), 427(64), 432(64), 442, 443
 Calderon, J. L., 153(16), 202
 Calligaris, M., 344(21, 22, 23, 24, 27), 347(21, 24), 348(23), 402(28, 29), 442
 Campbell, I. G., 221(77), 251
 Campbell, J. M., 255(10), 256(12), 257(9), 264(10, 12), 265(10), 270(8, 9, 10), 272(9, 10), 274(11, 12), 275(9, 10, 11, 12), 276(9), 278(10), 279(11, 12), 280(12), 281(206), 283(8), 285(9, 10), 286(12, 205), 287(9, 10), 323, 329
 Camus, A., 334(123), 348(123), 444
 Capka, M., 310(45a), 324
 Capron-Cotigny, G., 119(57), 121(56), 141
 Cardin, D. J., 255(47, 48), 267(47), 268(46), 278(49), 285(49), 288(49), 324
 Carey, N. A. D., 285(50), 324
 Cariati, F., 59(55), 82
 Carlson, T. A., 212, 246, 250
 Carrick, A., 92(57), 141
 Carturan, G., 138(57a), 141

Casey, C. P., 108(60), 122(60), 123(58, 59), 141
 Cassar, L., 135(61), 141, 188(15), 202
 Caulton, K. G., 24, 25, 82
 Cawse, J. N., 130(70a), 141
 Cercek, B., 174(17), 202
 Cerny, M., 310(45a), 324
 Cesari, M., 344(30), 348(30), 378(30), 442
 Cetinkaya, B., 268(46), 324
 Chalk, A. J., 118(62), 131(62), 141, 257(56, 57), 258(56, 57), 259(51, 55), 265(57), 266(57), 267(55), 268(51), 270(51), 273(52), 277(55), 298(54, 55), 299(52, 55, 57, 130), 300(54, 55), 301(51, 55, 129), 303(51, 54, 55), 304(51, 52, 54, 55), 305(52, 54, 55), 306(52, 54, 55, 56, 57, 130), 307(53, 54, 58), 308(53, 55), 309(52, 53), 324, 325, 327
 Challenger, F., 172(18), 202
 Chalmers, A. A., 285(38), 324
 Chalmers, T. A., 207, 211, 251
 Chambers, D. B., 287(59), 288(59), 325
 Chandler, P. J., 286(2), 323
 Chang, Y. F., 137(206), 144
 Chapovsky, Yu. A., 129(185, 186, 187, 190), 144
 Charles, R., 259(131), 303(131), 304(131), 327
 Charley, L. M., 45, 47(5), 61, 81
 Chatt, J., 42(8, 9), 45(8), 46(8, 9), 60, 80(8, 9), 81, 82, 92(39), 137(38, 39, 63), 138(38, 39), 139(39), 140, 141, 161, 202, 259(63, 64, 65), 260(63, 65), 264(63), 265(61), 266(62, 63), 267(62, 63), 268(65), 269(65), 271(65), 272(64), 273(64), 274(63), 276(63), 278(65), 279(64), 286(63, 64), 288(63), 290(56), 293(65), 325, 342(31), 442
 Chaudhari, F. M., 130(64), 141
 Cheney, A. J., 269(245), 330
 Chi-Minh, L., 246(64), 251
 Chock, P. B., 359(32), 381(32), 382(32), 408(32), 410(32), 442
 Christian, D. F., 61(37), 67(37), 82
 Chukovskaya, E. T., 299(175a), 328
 Church, M. J., 36(38, 39), 77, 82
 Churchill, M. R., 91(65), 141
 Citron, J. D., 308(67), 325
 Claeys, E. G., 286(99, 100), 326

- Clark, H. C., 34, 36(41), 42, 46(42), 76(42), 79(41), 82, 89(67), 137(66), 138(66), 141, 278(34), 279(33), 285(50), 324
- Clarke, D. A., 364(33, 34), 386(33), 388(33, 34), 390(33), 408(33), 411(33), 412(33), 415(33), 442
- Cleland, A. J., 262(68, 110, 183), 264(183), 290(110), 296(183), 325, 326, 328
- Clemens, J., 73(43), 74(43), 82
- Clemmit, A. F., 259(69, 71), 265(69, 71), 273(69, 71), 274(71), 276(69, 71), 277(71), 278(71), 303(71), 325
- Closson, R. D., 88(70), 118(70), 122(69, 70), 126(70), 141
- Coates, G. E., 263(72), 278(73), 318(73), 325
- Cocevar, C., 390(42), 407(41), 413(41), 421(41), 424(41), 442
- Cockerill, A. F., 152(9), 164(9), 202
- Cockle, S., 348(35), 384(35), 442
- Cocton, B., 185(19), 202
- Coffey, C. E., 132(68), 141
- Coffield, T. H., 88(70), 112, 118(70), 122(69, 70), 126(70), 141
- Coleman, R. A., 15(60), 16(60), 20
- Collier, M. R., 310(78), 311(73a, 76, 77, 78), 312(73a, 74, 75, 76, 78), 313(76, 78), 314(76, 77, 78), 315(73a, 76, 77, 78), 316(73a, 74, 75, 78), 317(74), 319(73a, 75, 77, 78), 320(74, 75, 76, 77, 78), 321(77, 78), 322(73a, 75, 77, 78), 325
- Collins, C. H., 220(99), 226(99), 227(99), 228(99), 238(99), 239(99), 252
- Collins, K. E., 220(99), 226(99), 227(99), 228(99), 238(99), 239(99), 252
- Collman, J. P., 130(70a, 215a), 136(72), 137(71), 141, 145, 268(81), 269(81), 301(78a, 79), 304(79), 325
- Colonomos, M., 247(19), 250
- Connolly, P. J., 435(24a), 442
- Connor, J. A., 53(44), 82
- Cook, C. D., 139(73), 141, 277(82), 306(82), 310(83), 325
- Cooke, M., 118(47), 140, 257(43), 275(43), 324
- Cooke, Jr., M. P., 130(74), 141
- Coombes, R. G., 160(20), 202
- Cooper, R., 151(21), 202
- Cope, A. C., 334(36), 442
- Cope, I. S., 148(104), 173(104), 204
- Corain, B., 268(37), 324
- Corey, E. J., 152(22), 155(22), 202
- Corey, E. R., 281(127), 289(30), 324, 327
- Corriu, R. J. P., 308(84), 325
- Cossee, P., 90(75), 141
- Costa, G., 133(76, 77), 141, 342(38, 39, 43, 47, 49), 345(16, 40, 43, 47, 49, 83), 346(16), 347(16), 350(47, 48, 83), 351(40, 42, 43, 45), 354(16), 355(40, 43), 356(16, 46), 357(43), 361(37, 45), 366(16, 39, 42, 45, 46, 48, 50), 367(42, 46, 48, 50), 372(16, 44), 375(40, 49), 376(40, 44, 49, 50, 83), 377(37, 43, 47, 50), 378(16, 37, 43, 47, 50), 379(16, 37, 38, 43, 44, 50), 380(16, 44), 381(44), 386(40, 43), 387(42, 46), 388(16, 40), 43, 46), 389(40, 43), 390(41, 42, 46, 47, 49), 391(16, 50), 392(40, 43, 47), 393(38, 44), 396(83), 405(37, 44), 407(41, 47), 413(41), 414(45), 417(47, 49), 421(41), 424(41), 429(44), 432(42, 45, 49), 433(51), 441, 442, 443
- Costea, T., 230(20), 250
- Cotton, F. A., 59, 80(45), 82, 93(78), 94(50, 51, 52), 101, 105(50, 51), 107(50, 51), 108(50, 51), 109, 113(78), 120(78), 122(50, 51), 123(52), 124(51), 125(50, 51, 52), 141, 149(25), 150, 151(25), 152(25, 169), 153(16, 24), 164(26), 202, 206, 231(68), 251, 283(3), 285, 289(186), 291(3), 301(87), 323, 325, 328
- Cotton, J. D., 256(35), 257(35), 288(35), 324
- Cox, A. P., 150(160), 206
- Cozens, R. J., 378(53, 128), 430(53, 128), 443, 445
- Cradock, S., 259(27), 260(27), 266(27), 268(27), 270(27), 271(27), 274(27), 277(27), 286(27), 302(27), 303(27), 324
- Craig, P. J., 65(28), 82, 92(8), 94(79, 80, 81), 97(80, 81), 99, 100(79), 101(80, 81), 113(80), 119(79, 80, 81), 120(80, 81), 133(40), 139, 140, 141, 336(17), 345(17), 378(17), 380(17), 442
- Criegee, R., 147, 169(28), 170(28), 175(27), 180(27), 202

Criswell, T. R., 122(207), 144
 Crociani, B., 34, 35, 39(46, 49), 44(46),
 46(25, 48), 66(29), 74(25, 29, 30, 49),
 75(25, 47), 80(25), 82, 135(87), 141
 Crook, J. R., 59(78), 60(78), 83
 Cross, R. J., 138(82), 141, 254(40, 123),
 292(40), 318(35a), 324, 327
 Crumbliss, A. L., 350(52), 367(52), 368(52),
 369(52), 443
 Cundy, C. S., 260(90), 262(89, 90), 263(90),
 269(90), 286(90), 293(89), 294(88),
 308(88, 89), 315(90), 325
 Cunico, R. F., 324
 Curtis, M. D., 256(91), 258(92), 263(91),
 264(92, 92a), 278(91), 325

D

Dainton, F. S., 174(10), 202
 Dalton, J., 255(94), 256(94), 257(95),
 258(95), 262(96), 286(93, 93a, 97), 326
 Danforth, R. H., 158(147), 159(147),
 169(147), 170(150), 172(147), 205
 Dart, J. W., 36(50), 64(50), 65(50), 66(50),
 67(50), 82
 Dartiguenave, M., 65(51), 82
 Dartiguenave, Y., 65(51), 82
 Davidson, J. M., 161(29), 162, 202
 Davidson, P. J., 126(33), 140, 293(98),
 312(98), 315(98), 320(98), 326
 Davies, N. R., 161(1), 202
 Davis, J. W., 102(83), 141
 Davis, R. E., 73(43), 74(43), 82
 Day, J. M., 234(22), 250
 Day, P., 364(54), 365(54), 387(54), 443
 Deacon, G. B., 155(30), 164(30), 202, 378
 (53, 128), 430(53, 128), 443, 445
 de Caluwe, R. M., 286(100), 326
 de Charenteney, F., 258(60), 299(60),
 304(60), 305(60), 309(60), 325
 Deeming, A. J., 135(84), 137(85, 86), 141
 Deganello, G., 95(233), 135(87, 233), 141,
 145, 254(243), 330
 Dehnicke, K., 155(106), 204
 de Jong, I. G., 218(44, 47), 219(46), 226(44,
 46), 229(44, 45, 46), 230(44, 47), 231
 (44), 232(48), 233, 238(44), 239(48),
 240(44, 45), 243(44), 247(43), 248(45),
 250

Dekker, M., 51(22), 82
 Delbeke, F. T., 286(99, 100), 326
 de Maine, M. M., 239(55), 251
 Demidov, A. M., 209(3), 210(3), 249
 Denisov, F. S., 256(193), 286(193), 328
 Dennis, L. M., 155(136), 205
 Dent, S. P., 308(101), 326
 Dent, W., 289(102), 326
 de Paulet, A. C., 185(19), 202
 de Savorgnani, E., 356(46), 366(46), 367
 (46), 387(46), 388(46), 390(46), 442
 Desgrez, A., 192(31), 202
 Deutsch, E., 353(147, 148), 354(147),
 355(148), 366(147), 367(147), 368
 (147), 369(147), 370(147), 371(147),
 372(147), 373(147), 374(147), 375
 (147), 378(147), 388(147), 417(147),
 445
 Dickson, R. S., 72(52, 52a), 82
 Dilworth, M. J., 426(71), 443
 Dimroth, P., 169(28), 170(28), 202
 Dirreen, G. E., 27(154), 54(154), 55(154),
 56(154), 85
 Distefano, G., 53, 82, 83
 Dixon, K. R., 42(40), 82
 Dobbs, B., 133(40), 140, 336(17), 345(17),
 378(17), 380(17), 442
 Dobson, G. R., 255(103), 277(103, 207),
 326, 329
 Dodd, D., 348(55), 369(55), 425(55), 443
 Dodson, R. W., 219(58), 223, 240(85),
 247(85), 251
 Doemeny, P. A., 53(138), 85
 Dolphin, D., 364(33, 56), 386(33, 56),
 388(33), 390(33, 56), 408(33), 411(33),
 412(33), 415(33), 432(57), 442, 443
 Domash, L., 8(10), 19
 Dornberger, E., 81(57), 83
 Douek, I. C., 95(88), 102(88), 135(88), 141
 Doveika, A., 209(3), 210(3), 249
 Dowden, D. A., 435(168), 446
 Doyle, J. R., 149(56), 152(56), 153(56), 203
 Drenth, W., 80(141), 85
 Dreys, H., 342(174), 346(174), 364(174),
 387(174), 425(174), 446
 Duchatsch, H., 133(128), 142
 Duc-Hiep, T., 342(174), 346(174), 364
 (174), 387(174), 425(174), 446
 Duncan, J. F., 234(21), 250

Duncanson, L., 289(102), 326
 Dunney, S., 298(25), 299(25), 324
 Duong, K. N. V., 353(129), 355(59),
 357, 358(59, 129), 369(58), 370(58,
 59, 129), 371(58, 129), 372(59), 373
 (59, 129), 388(59, 129), 392(129),
 405(58), 406(58), 411(129), 417(58,
 129), 430(58), 443, 445
 Dutton, H. J., 438(117), 444
 Dvolaitzky, M., 433(116), 437(116), 444
 Dvoryantseva, G. A., 149(110), 204
 Dymova, S. F., 373(18), 374(18), 442

E

Eaborn, C., 192(8), 202, 259(63, 64, 65,
 105a), 260(63, 65), 264(63), 265(61),
 266(62, 63), 267(62, 63), 268(65),
 269(65), 271(65), 272(64), 273(64),
 274(63), 276(63), 278(65), 279(64),
 286(63, 64), 288(63), 293(65), 294(88),
 298(105), 299(105), 300(105), 302
 (105), 308(88, 89, 101, 104), 312(74),
 313(74), 316(74), 317(74), 320(74),
 325, 326
 Eastmond, G. C., 51(12), 81
 Eastwood, K. M., 209(3), 210(3), 249
 Eaton, P. E., 135(61), 141, 188(15), 202
 Ebert, M., 174(17), 202
 Ebsworth, E. A. V., 259(27), 260(27),
 266(27), 268(27), 270(27), 271(27),
 274(27), 277(27), 282(106), 286(27),
 296(106), 302(27, 29), 303(27, 28),
 324, 326
 Edwards, L. M., 268(44), 324
 Edwards, P. A., 289(41), 324
 Edwards, R. R., 234(22), 250
 Efraty, A., 52, 83, 119(145), 132(146),
 143
 Elder, M., 261(108, 143), 290, 291(107),
 326, 327
 Elsom, L. F., 148(86), 149(87, 88), 204
 Emerson, K., 281(109), 282(109), 326
 Enemark, J. H., 40(54), 43(33, 34), 44(33,
 54), 45(99), 46(99), 61(99), 74(33, 34),
 80(33, 34), 82, 84
 Espenson, J. H., 367(1), 369(1), 371(1),
 397(1), 422(1), 441
 Evans, D., 135(89), 141

Evans, D. F., 151(98), 156(98), 165(98, 99),
 204
 Evans, G. O., 289(203a), 329

F

Fachinetti, G., 118(89a, 90a), 141
 Fantucci, P. C., 59(55), 82
 Faraglia, G., 164(32), 202
 Farkas, L., 190, 205
 Farmery, K., 351(60), 365(60), 387(60),
 432(60), 443
 Favero, G., 268(37), 324
 Favier, R., 183(38), 202
 Fear, C. M., 147(33), 202
 Fedin, E. I., 150(114), 151(114), 204
 Fedorov, L. A., 127(250), 145, 150(114),
 151(114), 204
 Fehlhammer, W. P., 41(19, 20), 80, 82
 Felder, P. W., 378(53, 128), 430(53, 128),
 443, 445
 Fennessey, J. P., 91(65), 141
 Fenske, R. F., 24, 25, 26(133), 55(133), 82,
 85
 Ferradini, C., 174(107), 204
 Fieldhouse, S. A., 262(68, 110, 183),
 264(183), 290(110), 296(183), 325,
 326, 328
 Filbey, A. H., 122(136), 123(136), 124(136),
 143
 Fink, W., 260(110a), 262(110a), 269(110a),
 310(110b), 326
 Fiorani, L. R., 164(32), 202
 Firth, R. A., 346(61), 413(61, 62), 417(61),
 420(61), 430(63), 443
 Fischer, E. O., 52, 57(56), 80(56), 81, 81,
 83, 118(90), 141, 149(34, 35), 150(36),
 151(21), 202, 232(8), 236(5, 6, 7, 8), 250
 Fischer, R. D., 81(159, 160), 85
 Fitzsimmons, B. W., 59(21, 65), 82, 83
 Floriani, C., 118(89a, 90a), 141, 342(64),
 345(64), 377(26, 64), 378(64), 386(26,
 64), 390(64), 392(64), 425(64), 427(64),
 432(64), 442, 443
 Foffani, A., 53(53), 82
 Fong, C. W., 88(91), 90(154), 142, 143
 Fontaine, C., 369(58, 68), 370(58), 371(58),
 405(58, 68), 406(58), 417(58), 430(58,
 68), 443
 Ford, M. E., 191(96), 204

Fowler, J. S., 163(89), 164(91), 171(91), 204
 Fox, J. P., 350(143), 367(143), 445
 Frasson, E., 150(37), 202
 Frazier, R. H., 53(138), 85
 Freeland, B. H., 262(68, 110, 183), 264
 (183), 290(110), 296(183), 325, 326, 328
 Freidlina, R. K., 299(175a), 328
 Freppel, C., 183, 185, 202
 Friedel, R., 289(186), 328
 Friedlander, G., 246(74), 251
 Friedman, S., 426(71, 72), 443
 Friedrich, W., 358(65, 66), 430(66), 443
 Fritz, H. P., 149(35), 150, 202, 203
 Fujimoto, H., 299(224), 301(224), 308
 (224), 329
 Fujita, K., 191(161), 206
 Fukui, S., 414(180), 420(67, 180), 425(180),
 426, 443, 446
 Furrer, J., 261(174), 286(174), 291(174),
 328

G

Gallay, J., 95(204), 144
 Gallivan, P. M., 13(45), 14(45), 19
 Gans, P., 59(21), 82
 Garrod, R. E. B., 59(17), 82
 Gaudemer, A., 353(129), 355(59), 357,
 358(59, 129), 369(58, 68), 370(58,
 59, 129), 371(58, 129), 372(59), 373(59,
 129), 388(15, 59, 129), 392(129), 405
 (58, 68), 406(58), 411, 414(15), 417(58,
 129), 430(58, 68), 441, 443, 445
 Gavin, Jr., R. M., 150, 205
 Gavrilova, L. D., 150(41), 203
 Gay, R. S., 289(203a), 329
 Geibel, K., 133(164), 143
 Giacobbe, T. J., 200(72), 203
 Giannotti, C., 369(58, 68), 370(58), 371
 (58), 405(58, 68), 406(58), 417(58),
 430(58), 443
 Gilman, H., 147, 148(43, 44, 45), 155(45),
 156(43), 162, 203, 260(111), 265(112),
 326
 Gilmore, C. J., 65(58), 83, 292(246), 330
 Gilson, D. F. R., 259(131), 303(131), 304
 (131), 327
 Gintis, D., 8(10), 19
 Glockling, F., 92(57), 141, 254(115a),
 258(113), 259(69, 71, 113, 114, 216),

263(72), 265(69, 71, 114), 267(216),
 269(113), 272(114), 273(69, 71, 114,
 115), 274(71, 114, 115), 276(69, 71,
 114, 115), 277(71, 114), 278(71),
 279(114), 285(114), 286(114, 115),
 287(59), 288(59), 303(71, 114), 304
 (114), 325, 326, 329
 Glushkova, V. P., 147, 162, 169(47, 48),
 195(49), 203
 Glyde, R. W., 95(92, 93), 98, 101(92),
 102(92), 104(92, 93), 115(94), 137(92,
 94), 138(93), 142
 Golding, B. T., 371(69), 372(69), 398(69),
 410(69), 415(69), 443
 Golubtsov, S. A., 310(4a), 323
 Gondal, S. K., 99(132), 143, 257(117),
 258(116, 117), 271(116, 117), 287(211),
 288(211), 326, 329
 Goodall, D. M., 350(48), 366(48), 367(48),
 442
 Gordon, H. B., 137(206), 144
 Gordus, A. A., 211(39), 250
 Gorsich, R. D., 261(118), 286(119), 326
 Gottsegen, A., 190(118), 205
 Gourlay, R. N., 334(36), 442
 Gracev, S. A., 236(60), 251
 Graham, W. A. G., 124(197), 133(106),
 135(106, 107, 196), 137(106, 198), 142,
 144, 255(148, 149, 150, 152, 153),
 256(148, 149, 150, 151, 152, 153,
 201), 258(121, 149, 150, 175, 196b),
 259(148, 196b), 261(26, 120, 142, 143),
 262(18, 148), 264(201), 266(151),
 268(150, 201), 280(152), 286(148, 151,
 153), 287(153), 289(203a, 203b), 290
 (202), 291(26), 292(148), 297(247),
 324, 326, 327, 328, 329, 330
 Gray, H. B., 65(51), 82
 Graziani, M., 138(57a), 141
 Greatrex, R., 61(59), 83
 Greco, A., 73(60), 83
 Green, M., 73(43, 60, 61), 82, 83, 92(8, 35),
 94(79, 80, 81, 97, 98), 97(80, 81, 97,
 98), 99, 100(79), 101(80, 81), 113(80,
 99), 118(47), 119(79, 80, 81), 120(80,
 81), 123(13, 15, 99), 124(13, 15, 35),
 125(16, 95, 96, 97), 127(98), 128(98),
 137(5), 138(175), 139(176), 139, 140,
 141, 142, 143, 257(43), 275(43), 324,

- 350(48), 366(48), 367(48, 70a), 442, 443
- Green, M. L. H., 51, 83, 119(100), 128 (100, 101, 103), 129(102), 130(101), 142, 269(122), 278(73), 318(73), 325, 326
- Greenwood, N. N., 61(59), 83
- Grevels, F.-W., 111(155), 143
- Griffith, W. P., 333(70), 341(70), 342(70), 346(70), 360(70), 381(70), 395(70), 396(70), 413(70), 443
- Grigg, R., 364(33, 34), 386(33), 388(33, 34), 390(33), 408(33), 411(33), 412 (33), 415(33), 442
- Groening, H. R., 225, 226(23), 227, 250
- Groll, H. P. A., 155(50), 203
- Groshev, L. V., 209(3), 210(3), 249
- Grossmann, G., 222(27), 224, 228(27, 36), 250
- Gryder, J. W., 219(58), 251
- Guest, J. R., 426(71, 72), 443
- Guttenberger, J. F., 53, 83
- Guy, R., 289(102), 326
- H**
- Haas, H., 69, 83
- Hagen, A. P., 255(124), 257(125, 189), 258(125, 126, 189, 210), 264(124), 273(124), 275(124), 280(124), 286 (125), 287(210), 288(124, 210), 289 (30), 324, 326, 328, 329
- Hagihara, N., 29(164), 39(164), 60(168), 65, 74(163, 164), 85, 90(244), 137(247), 145, 299(229), 306(229), 308(229), 310(229a), 330, 334(182), 446
- Hahne, R. M. A., 232(38), 250
- Haim, A., 350(73), 443
- Haines, L. I. B., 92(104), 142
- Hall, D., 59(65), 83
- Hallam, B. F., 231(28), 250
- Halpern, A., 221, 222, 243(75), 251
- Halpern, J., 135(61), 141, 188, 202, 333, 350(74), 356(75), 359(119, 144), 360 (118), 369(144), 374(144), 378(118), 379(118), 380(118, 119), 381(32, 74), 382(32, 75), 383(75), 389(119, 144), 390(118), 394(74), 395(75), 406(74), 408(32), 410(32, 75), 413(74), 414(75), 416(75), 421(74), 425(74, 75), 442, 443, 445
- Hamilton, J. A., 357, 382(94), 411, 416(94), 436(94), 438(94), 444
- Hamilton, R. S., 281(127), 327
- Hancock, R. I., 94(97), 97(97), 125(95, 96, 97), 142
- Hanna, J. A., 91(105), 118(105), 142
- Hanzlik, J., 351(76), 443
- Hara, M., 299(128), 308(128), 309(128), 327
- Harbottle, G., 218, 220, 224, 225, 226(23), 227, 228, 233, 241(29), 242(29), 243, 245, 246, 250, 252
- Hardt, P., 334(178), 336(178), 446
- Hargreaves, K., 51(12), 81
- Hargreaves, R. G., 125(36), 140
- Harris, C. B., 289(41), 324
- Harris, W. E., 289(36), 324
- Harrod, J. F., 118(62), 131(62), 141, 257(56, 57), 258(56, 57), 259(55, 131, 133), 265(57), 266(57), 267(55), 268 (133), 269(132, 133), 277(55), 290(56), 298(55), 299(55, 57, 130), 300(55), 301(55, 129, 132, 133), 303(55, 131, 132), 304(55, 131, 132, 133), 305(55, 132), 306(55, 56, 57, 130), 307(58), 308(55), 325, 327
- Hart, C. R., 156(51), 203
- Hart-Davis, A. J., 95(108), 102, 119(108), 120(108), 133(106), 135(106, 107), 137(106), 142, 261(120), 326
- Hartley, D., 285(134), 327
- Hartwell, G., 360(5), 383(5), 396(5), 441
- Haszeldine, R. N., 92(35), 94(37), 103(37), 105(37), 107(37), 108(37), 123(13, 15), 124(13, 15, 35), 125(14, 16, 37), 139, 140, 258(5, 135), 268(135), 271(135), 272(135), 273(135), 275(135), 277 (135), 280(135), 289(5), 291(5), 294 (248), 299(5, 135), 304(135), 305(135), 307(5), 318(248), 323, 327, 330
- Haward, R. N., 90(26), 140
- Hawks, III, G. H., 202(151), 205
- Hayashi, T., 260(240), 299(240), 310(240, 240b), 330
- Hayward, G. C., 350(78), 393(77), 398(77), 413(77), 414(77), 420(78), 443
- Heaton, B. T., 286(136), 287(136), 327
- Hébert, N. C., 15(57), 20

- Heck, R. F., 90, 92(114), 93(115), 94(118), 108(109), 109, 118(117), 131(41, 111, 117, 118, 120, 121, 122, 123), 132(110), 135(113), 137(112, 113), 138(116, 119), 140, 142, 272(137), 283(138), 307(138), 327, 336(79), 431(79), 443
- Heim, P., 11(32), 19
- Heimbach, P., 137(123a), 142, 334(178), 336(178), 446
- Hein, F., 254, 327
- Heitz, C., 216(32), 222, 247(33), 250
- Hengge, E., 255(140), 261(140), 327
- Henrich, E., 226(34), 228, 245, 246(34), 250
- Henry, P. M., 138(124), 142, 175(52), 177(53), 185(52, 54), 186, 203
- Herberhold, M., 57(101), 84
- Herlinger, A. W., 63, 83, 91(125), 133(125), 142, 367(80), 368(80), 429(80), 443
- Herr, W., 216(35), 250
- Hess, R. W., 32(144, 147), 33(144, 145), 37(146), 38(145, 146), 39(146), 40(147), 42(147), 44(146), 45(147), 46(147), 50(147), 57(146), 61(146), 68(147), 76(147), 77, 78, 79(144), 80(144, 147), 85
- Hetfleje, J., 310(45a), 324
- Heydkamp, W. R., 15(55), 20
- Heyman, D. A., 148(54a), 203
- Hieber, W., 122(22), 123(129), 125(127), 131(131), 133(126, 128, 130), 140, 142, 342(81), 443
- Higgins, C. R., 255(124), 264(124), 273(124), 275(124), 280(124), 288(124), 326
- Highsmith, R. E., 268(140a), 327
- Higson, B. M., 344(4), 349(4), 361(4), 378(4), 381(4), 391(4), 441
- Hill, G. C., 258(113), 259(113), 269(113), 326
- Hill, H. A. O., 332(85, 86), 341(86, 87), 342(85, 86), 345(82, 83), 346(61), 348(35, 88), 350(48, 78, 83), 364(54), 365(54), 366(48), 367(48), 371(81a), 376(82, 83), 377(82), 384(35, 88), 387(54), 389(2), 393(77), 397(83), 398(77), 413(61, 62, 77), 414(77), 417(61), 420(61, 78), 422(84), 423(84), 424(2, 84), 427(2, 3), 430(63), 441, 442, 443, 444
- Hill, N. J., 311(189a), 312(189a), 314(189a), 315(189a), 318(189a), 319(189a), 321(189a), 322(189a), 328
- Hillman, M., 223(36), 232(38), 240(37), 250
- Hines, L. F., 117(131a, 218), 138(131a, 218), 142, 145
- Hiroto, K., 47(124), 48(118, 120, 123, 124), 71(67), 80(124), 83, 84
- Hitch, R. R., 99(132), 143
- Ho, R. K. Y., 369(160), 422(160), 423(160), 445
- Hodgkin, D. C., 332, 341(115), 444
- Höfler, M., 119(158a), 121(158a), 123(129), 127(158a), 142, 143
- Hogenkamp, H. P. C., 346(90), 404(134), 409, 410, 414(91a), 415(7, 8, 9, 91a), 420(89), 433(91), 441, 444, 445
- Holland, H. L., 371(69), 372(69), 398(69), 410(69), 415(69), 443
- Holland, R. J., 351(149), 352(149), 355(149), 356(149), 439(150), 445
- Holmes, S., 433(91), 444
- Hooton, K. A., 259(114, 141), 265(114, 141), 270(141), 272(114), 273(114, 115), 274(114, 115), 276(114, 115), 277(114), 279(114), 285(115), 286(114, 115), 303(114), 304(114), 326, 327
- Horn, U., 371(69), 372(69), 398(69), 410(69), 415(69), 443
- Horowitz, R. H., 8(14), 19
- Houk, L. W., 119(147), 121(147), 133(148), 143
- Hoyano, J. K., 261(26, 142, 143), 262(18), 290(18), 291(26), 323, 324, 327
- Hsieh, A. T. T., 69(68), 70(68), 79(68), 83
- Hseiung, C., 211, 250
- Hsiung, H., 211(39), 250
- Hübel, W., 289(172), 328
- Hull, H., 149(55), 203
- Humpfer, K., 156(146), 205
- Hunt, C. C., 149(56), 152(56), 153(56), 203
- Hunt, J. D., 157(90), 163(89), 164(90, 91), 165(153), 171(91), 177(92), 178(92), 187(92), 196(93), 204, 205
- Huq, F., 312(144, 145), 314(144, 145), 316(144, 145), 319(144, 145), 327
- Hurley, C. R., 119(100), 128(100), 142

I

- Ibekwe, S. D., 259(63), 260(63), 264(63), 265(61), 266(62, 63), 267(62, 63), 274(63), 276(63), 286(63), 288(63), 290(146), 315(145a), 325, 327
- Ibers, J. A., 72(52, 52a, 139), 82, 85, 258(206), 281(184, 191), 282(176, 184, 191), 283(184, 191, 206), 305(191), 328, 329
- Ichikawa, K., 8(17), 19, 189(162), 191(161), 199(162), 206
- Ignatowicz, A. K., 122(207), 144
- Iguchi, M., 333(92, 93), 434, 444
- Ikegami, K., 10(25), 19
- Ikegami, S., 10(26), 19
- Illingworth, S. M., 262(18), 290(18), 323
- Ingemanson, C. M., 53, 81
- Ingold, C. K., 156(51), 203
- Ingraham, L. L., 350(143), 367(143), 445
- Innorta, G., 53, 82, 83
- Inubushi, Y., 49(131), 84
- Ioganson, A. A., 122(181, 182, 184), 124(4), 125(4, 184), 126(181, 182, 183, 184), 139, 144 (see Johannsson, A. A.)
- Igbal, M. Z., 122(44), 125(33, 44), 140
- Ireland, P. R., 281(109), 282(109), 326
- Irion, E., 425(13), 441
- Irving, H. M. N. H., 59(21), 82
- Isaikina, T. A., 126(248), 145
- Isbell, H. S., 161(63), 203
- Ishag, M., 128(151), 143, 256(164), 263(164), 288(164), 312(164), 319(164), 321(164), 327
- Ishida, V., 51(135), 85
- Ishikawa, M., 263(147), 327
- Ito, Y., 22, 47(124), 48(118, 119, 120, 123, 124, 128, 129, 132), 49(119a, 121, 125, 126, 130, 131), 80(124, 132), 84, 85
- Itoh, M., 15(63), 20

J

- Jach, J., 224(40), 250
- Jackman, L. M., 357, 382(94), 411, 416(94), 436(94), 438(94), 444
- Jacko, M. G., 156(57), 203
- Jacobs, W. J., 42(40), 82
- Jakubinek, H., 229(42), 232(41, 42), 233, 248(41, 42), 250
- James, T. A., 51, 84
- Janshen, J., 169(133), 205
- Japanese Patent, 65(173), 74(174), 86, 195(58), 203
- Jardine, F. H., 304(197), 305(197), 329
- Jauhal, G. S., 139(73), 141, 277(82), 306(82), 310(83), 325
- Jenks, C. H., 216(94), 252
- Jensen, F. R., 353, 370(95), 371(95), 372(95), 388(95), 444
- Jernigen, R. T., 255(103), 277(103), 326
- Jetz, W., 255(148, 149, 150, 152, 153), 256(148, 149, 150, 151, 152, 153), 258(121, 149, 150), 259(148), 262(148), 266(151), 268(150), 280(152), 286(148, 151, 153), 287(153), 292(148), 326, 327
- Job, E., 256(171), 259(171), 328
- Johannsson, A. A., 91(6), 139, 286(154), 327 (see Ioganson, A. A.)
- Johnson, A. W., 356(97), 364(33, 34, 56), 384(97), 385(97), 386(33, 56, 96), 388(33, 34), 390(33, 56), 406(167), 408(33), 411(33), 412, 415(33), 432(57), 442, 443, 444, 446
- Johnson, B. F. G., 153(59), 203
- Johnson, M. D., 160(20, 60), 175(60), 202, 203, 346(100, 101), 348(55), 357(102), 368(98), 369(55), 370(99), 382(100, 101), 383(9, 100, 101, 102), 393(99, 101), 396(100, 101), 397(101, 102), 398(99), 399(101, 102), 402(102), 406(100, 102), 410, 411, 413(99), 414(100, 101, 102), 416(101, 102), 420(100, 102), 423, 424(8), 425(9, 55), 429(100, 102), 430(98), 438(102), 441, 443, 444
- Johnson, N. P., 137(63), 141
- Johnston, R. D., 55(69), 56(69), 83
- Jolly, P. W., 125(133), 137(123a), 142
- Jones, C. J., 136(7), 139
- Jones, E. M., 53(44), 82
- Jones, R. G., 148(43, 44, 45), 155(45), 156(43), 203
- Joshi, K. K., 37, 54, 55, 60(70, 71), 83, 93(134), 125(134), 142
- Jovanovic, B., 43(73), 83, 312(74), 313(74), 316(74), 317(74), 320(74), 325

K

- Kabalka, G. W., 15(54, 61), 20
 Kabbe, H.-J., 147, 169(61), 173(61), 177(61), 180(61), 203
 Kaesz, H. D., 122(135), 125(135), 143, 249(49), 250, 261(26), 291(26), 324
 Kagan, E. G., 299(204), 301(204), 329
 Kahlen, N., 329
 Kahn, M., 216(79), 251
 Kahn, O., 256(156), 257(155, 156), 258(155, 156), 266(156), 272(156), 285(157), 288(156), 327
 Kajimoto, T., 35, 74(74), 83
 Kanaya, I., 130(222), 145
 Kanellakopulos, B., 81(57, 159, 160), 83, 85
 Kanellakopulos-Drossopulos, W., 224(51), 231, 239(50), 240(50), 245(51), 249(51), 251
 Kapoor, P. N., 119(147), 121(147), 143, 259(63, 64, 65, 105a), 260(63, 65), 264(63), 266(62, 63), 267(62, 63, 158), 268(65), 269(65), 271(65), 272(64), 273(64), 274(63), 276(63), 278(65), 279(64), 286(63, 64), 288(63), 293(65), 325, 326, 327
 Kapoor, R. N., 129(149), 133(148), 143, 153(65), 203
 Kaska, W. C., 64(75, 81), 83
 Kataoka, N., 64(76, 77), 83
 Katz, T. L., 151(62), 154(62), 203
 Kawaii, R., 399(127), 445
 Kay, I. T., 386(96), 444
 Keblys, K. A., 122(136), 123(136), 124(136), 143
 Keier, N. P., 351(104), 387(104), 444
 Keim, W., 134(137), 143, 315(158a), 327, 334(178), 336(178), 446
 Keith, R. E., 59(78), 60(78), 83
 Kelly, M., 53, 83
 Kembball, C., 435(24a), 442
 Kennedy, F. S., 427(3), 441
 Kennedy, J. W., 246(74), 251
 Keppie, S. A., 255(47, 48), 267(47), 269(160), 278(49), 285(49, 159), 288(49), 324, 327
 Kettle, S. F. A., 262(161, 162), 289(161), 290(162), 327
 Khan, I., 262(161, 162), 289(161), 290(162), 327
 Kharasch, M. S., 161(63), 203
 Kharasch, N., 171, 206
 Kiefer, G. W., 53(138), 85
 Kienle, P., 216(52), 251
 Kienzle, F., 159(152), 164(91), 165(153), 171(91, 152), 177(92), 178(92), 187(92), 204, 205
 Kierosawa, H., 36(41), 79(41), 82
 Kim, C. K., 223(36), 250
 Kim, J. Y., 353(103), 415(103), 434(103), 436(103), 438(103), 444
 Kimball, M. E., 64(75, 81), 83
 King, N. N., 350(11), 441
 King, R. B., 29(83), 52, 83, 111(141), 119(144, 145, 147), 121(141, 147), 122(135, 139, 140), 124(143, 144), 125(135, 150), 126(138, 140, 141), 128(142, 143, 144, 151), 129(149), 130(152), 132(146), 133(148), 143, 153(64, 65), 203, 256(163, 164), 263(164), 272(163), 287(163), 288(164), 312(164), 319(164), 321(164), 327
 Kingston, B. M., 255(48, 165, 166), 261(166), 264(166), 268(166), 275(166), 276(166), 278(166), 282(166), 285(159), 311(76), 312(75, 76), 313(76), 314(76), 315(76), 316(75), 319(75), 320(75, 76), 322(75), 324, 325, 327, 328
 Kinoshita, H., 49(119a, 125, 126, 130), 84
 Kira, M., 265(214), 329
 Kirch, L., 131(153), 143
 Kirsch, J. L., 289(41), 324
 Kiso, Y., 259(167), 299(173), 305(173), 308(173), 309(173), 328
 Kitching, W., 88(91), 90(154), 142, 143, 161(66, 67), 162(66, 67), 173(66), 175(66), 177(68), 181(66), 203
 Kitoh, R., 189(162), 191(161), 199(162), 206
 Klein, W., 433(12), 438(12), 441
 Klopman, G., 162, 203
 Klose, U., 256(171), 259(171), 328
 Knebel, W. J., 32(147), 40(147), 41(84, 149), 42(147), 45(147), 46(147), 50(147), 68(147), 76(147), 77, 78, 79(84, 149, 150, 151), 80(147), 83, 85
 Knights, E. F., 14(49), 19
 Knowles, P. J., 269(122), 326
 Knox, G. R., 51(22), 82, 130(64), 141

- Knox, S. A. R., 257(6, 168, 169, 170), 262(39), 266(169, 170), 267(169), 269(169), 272(6, 169), 273(6, 168, 169, 170), 276(6), 278(169), 283(6) 288(169), 292(39), 323, 324, 328
- Kobayashi, S., 47(124), 48(118, 119, 120, 123, 124, 128), 49(121), 80(124), 80
- Koch, H. J., 132(210), 144
- Koch, W., 196, 206
- Kocheshkov, K. A., 147, 148(111), 162, 169(47, 48, 85, 129), 174(85), 195(49), 203, 204, 205
- Kochetkova, N. S., 149(110), 150(114), 151(113, 114), 152(112, 115, 116), 153(113, 115), 154(113, 114), 204
- Kochi, J. K., 172(70), 174(70), 177(70), 203
- Koelliker, U., 152(22), 202
- Koerner von Gustorf, E., 111(155), 143
- Kohll, C. F., 138(173), 143
- Kohnle, J., 368(151), 369(151), 370(151), 372(151), 388(151), 390(151), 445
- Kojima, H., 310(229a), 330
- Kolc, J., 247(53), 251
- Kolobova, N. E., 91(6), 122(178, 179, 180, 181, 182, 184), 124(4), 125(4, 184), 126(181, 182, 183, 184, 248), 139, 144, 145, 153(108, 109), 204, 256(193, 194), 286(154, 193), 327, 328
- Kon, H., 64(76, 77), 83
- Kopylova, L. I., 310(233a), 330
- Kordosky, G., 161(124), 174(124), 180(124), 205
- Korenowski, T. F., 125(150), 143
- Korte, F., 433(12), 438(12), 441
- Kovredov, A. I., 126(248), 127(250), 145
- Kozikowski, J., 88(70), 118(70), 122(69, 70), 126(70), 141
- Kraihanzel, C. S., 102(83), 113(157), 114(156), 122(157), 123(156, 157, 158), 124(166), 141, 143, 285, 325
- Kranz, H., 133(164), 143
- Kratel, G., 258(216a), 267(216a), 329, 388(153), 445
- Kraus, S., 137(33a), 140
- Kröner, M., 334(178), 336(178), 446
- Kronrad, L., 247(53), 251
- Kruck, T., 119(158a), 121(158a), 127(158a), 143, 256(171), 259(171), 328
- Krüerke, U., 289(172), 328
- Kruglaya, O. A., 254(234), 255(234), 330
- Kruse, W., 173(71), 186, 203
- Kubota, M., 105(160), 109(160), 110, 136(159, 160), 137(159), 143
- Kuehne, M. E., 200(72), 203
- Kumada, M., 259(167), 260(240), 263(147), 299(173, 240), 305(173), 308(173, 240a), 309, 310(240, 240b, 240c), 327, 328, 330
- Kummer, D., 261(174), 286(174), 291(174), 328
- Kummer, R., 258(121, 175), 326, 328
- Kundo, N. N., 351(104), 387(104), 444
- Kurek, J. T., 178(11), 202
- Kurosawa, H., 148(73), 155(73), 156(73), 157(73), 160(73, 74, 75), 174(74, 75, 76), 175(75), 203
- Kuz'mina, N. A., 299(175a), 328
- Kwan, T., 353(103), 360(125), 396(125), 415(103), 434(103), 435(170), 436(103, 171), 437(124), 438(103, 172, 173), 444, 445, 446
- Kwiatek, J., 333, 336(105), 342(109), 353(105), 355(105), 357(105), 358(105), 359(105, 108), 381(105, 108, 109, 110, 111), 382(105, 108, 109, 110), 383(105, 108), 394(108), 395(105, 107, 109), 396(105), 398(105), 399, 400(109), 407, 409(105), 410(105, 109), 413(105, 110), 414(105, 109, 110), 415(105), 416(108), 425(109), 428, 429, 430(105, 111), 432(105, 109), 434(108), 435(105, 107, 109), 436(105, 106, 108, 109), 437(105, 108), 438(105, 107), 444

L

- Lane, C. F., 15(53), 16(66), 20
- LaPlaca, S. J., 282(176), 328
- Lappert, M. F., 29(84a), 83, 90, 143, 255(47, 48, 165, 166), 256(177), 260(90), 261(166), 262(89, 90, 177), 263(90), 264(166), 267(47), 268(46, 166, 177), 269(90, 160, 177), 275(166), 276(166), 278(49, 166), 282(166), 285(49, 159), 286(90), 288(49), 293(89, 98, 177), 294(88, 177), 296(177), 299(178), 308(88, 89), 310(78, 178), 311(76, 77, 78, 176a), 312(74, 75, 76, 78, 98), 313(76,

- 78), 314(76, 77, 78, 176a), 315(76, 77, 78, 90, 98, 145a, 176a), 316(74, 75, 78), 317(74), 318(75, 77, 78), 320(74, 75, 76, 77, 78, 98), 321(77, 78), 322(75, 77, 78), 324, 325, 326, 327, 328
- Larkin, G. A., 36(85), 76(85), 77(85), 83
- Larock, R. C., 15(56), 20
- Larson, Q. V., 216(94), 252
- Latimer, W., 174(77), 203
- Lau, P. T., 254(242), 330
- Lauberlau, P., 81(159), 85, 236(5, 6), 250
- Lawlor, J. M., 357, 382(94), 411, 416(94), 436(94), 438(94), 444
- Lawson, D. N., 134(9), 139
- Lee, A. G., 148(78, 79), 155(82), 156(78, 80), 157(78, 79), 160(79), 164(81), 175(79), 185(79), 203, 282(106), 296(106), 326
- Lee, J. B., 177(83), 181(83), 183(83), 203
- Lee, L. P., 63, 85, 367(154), 368(154), 369(154), 370(154), 371(154), 372(154), 374(154), 375(154), 388(154), 405(154), 417(154), 418(154), 421(154), 445
- Legzdins, P., 153(16, 24), 202
- Leighton, R. A., 208(59), 251
- Lemal, D., 254(203), 256(203), 263, 301(203), 329
- Lenhert, P. G., 332(114), 341(114, 115), 344(112, 113, 114), 347(112), 348(114), 398(112), 444
- Leoni, R., 58(26), 82
- Leonav, E. V., 150(114), 151(114), 154(117), 204
- Lepel, W. H., 80(103), 84
- L'Eplattenier, F., 131(162, 163), 143
- Leslie, W. B., 216(94), 252
- Levin, C., 161(124), 174(124), 180(124), 205
- Levitin, I. Y., 370(175), 424(175), 433(116), 437(116), 444, 446
- Levshenko, A. V., 236(63), 251
- Lewis, D. F., 50(86), 83
- Lewis, G. J., 368(98), 430(98), 444
- Lewis, J., 282(179), 285(38), 324, 328
- Lewis, T., 153(59), 203
- Li, G. S., 298(25), 299(25), 324
- Libby, W. F., 219(54), 251
- Licari, T., 351(42, 45), 361(45), 366(42), 367(42), 387(42), 390(42), 414(45), 432(42, 45), 442
- Liebig, L., 119(158a), 121(158a), 127(158a), 143
- Light, J. R. C., 287(59), 288(59), 325
- Lindner, E., 133(126, 130, 164), 142, 143
- Lindsell, W. E., 51, 83
- Lippard, S. J., 50(86), 83
- Littler, J. S., 195(84), 204
- Litzow, M. R., 278(49), 285(49), 288(49), 324
- Lloyd, M. K., 36(50), 64(50), 65(50), 66(50), 67(50), 82
- Loader, P. L., 125(14), 140
- Lodewijk, E., 138(165), 143
- Lodochnikova, V. I., 169(85), 174(85), 204
- Lokshin, B. V., 127(250), 129(185, 190), 144, 145, 286(154), 327
- Long, K. M., 346(131), 350(131), 365(131), 376(131), 388(131), 405(131), 406(131), 414(131), 445
- Lovie, J. C., 308(20), 324
- Ludwick, L. H., 346(116a), 367(116a), 368(116a), 444
- Lukehart, C. M., 93(78), 113(78), 120(78), 141
- Lukevits, E. Y., 254(180), 298(180), 299(180), 328
- Luk'yanova, R. V., 152(116), 204
- Lux, F., 81(87), 83
- Lyons, J. E., 257(223), 258(223), 299(224), 301(224), 304(223), 308(67, 223, 224), 325, 329

M

- Maasböl, A., 118(90), 141
- Mabrouk, A. F., 438(117), 444
- McBride, B. C., 365(117a), 444
- McClellan, W. R., 122(171), 143
- McCleverty, J. A., 36(50), 51, 64(50), 65(50), 66(50), 67(50), 82, 84, 118(172), 119(172), 143
- McClin, M. L., 223(90, 91), 247(90), 251, 252
- MacDiarmid, A. G., 255(31), 256(181, 191a), 257(13, 14, 117, 125, 182), 258(13, 14, 116, 117, 125, 126, 182,

- 210), 261(192, 192a), 264(31, 192), 265(31), 266(31), 268(140a), 271(116, 117), 272(31), 273(31, 182), 274(13, 14, 182, 191a), 278(13), 280(17), 286(125), 287(210, 211), 288(210, 211, 212, 213), 289(30, 212), 296(192, 192a), 299(13, 14), 306(13, 14), 307(13, 14), 308(182), 323, 324, 326, 327, 328, 329
- McDowell, M. V., 257(117), 258(116, 117, 210), 271(116, 117), 287(210, 211), 288(210, 211, 212, 213), 289(212), 326, 329
- McFarlin, R. F., 11(30), 19
- McGillivray, G., 158(147), 159(147), 164(91), 169(147), 171(91), 172(147), 192(148), 204, 205
- McGregor, A., 259(216), 267(216), 329
- McKenzie, E. D., 344(4), 349(4), 361(4), 378(4), 381(4), 391(4), 441
- McKillop, A., 148(86, 154, 155), 149(87, 88), 157(90), 158(147, 149), 159(147, 152), 163(89), 164(90, 91), 165(153), 169(147), 170(150), 171(91, 152), 172(147, 156), 177(92), 178(92), 187(92), 190(95), 191(95, 96), 192(148), 193(94), 195(94), 196(93), 199(97), 200(157), 201(158), 202(511), 204, 205, 206
- McQuillin, F. J., 135(205), 144
- McWeeny, R., 281(188), 328
- Madan, V., 353(95), 370(95), 371(95), 372(95), 388(95), 444
- Maddock, A. G., 59(17), 82, 208, 216, 221, 238(56), 239(55), 246, 251
- Mador, I. L., 395(107), 434(107), 435(107), 436(106, 107), 438(107), 444
- Mague, J. T., 134(9, 10), 135(10), 139
- Maher, J. P., 64(88), 83, 151(98), 156(98), 165(98, 99), 204, 333, 350(74), 356(75), 359(75), 381(74), 382(75), 383(75), 394(74), 395(75), 406(74), 410(75), 413(74), 414(75), 416(75), 420(74), 425(74, 75), 443
- Maitlis, P. M., 161(100), 204
- Makarova, L. G., 111(189), 121(189), 129(185, 186, 188, 190), 144
- Malatesta, L., 21, 22(90), 26, 41(90), 43(90), 49, 52(90), 54, 58(89), 64(90), 65(90), 66(90), 68, 70(90), 76(90), 79(90), 83
- Malathi, N., 59(91), 83
- Malek, P., 247(53), 251
- Mann, B. E., 68(92, 93), 83, 269(245), 330, 346(61), 348(35), 384(35), 413(61), 417(61), 420(61), 442, 443
- Mann, C. D. M., 262(110, 183), 264(183), 290(110), 296(183), 326, 328
- Manojlovic-Muir, L., 43(73), 83, 268(46), 281(184), 282(184), 283(184), 312(74), 313(74), 316(74), 317(74), 320(74), 324, 325, 328
- Manzer, L. E., 34, 46(42), 76(42), 82
- Maples, P. K., 113(157), 114(156), 122(157), 123(156, 157, 158), 124(166), 143
- Margrave, J. L., 263(185), 328
- Markby, R., 289(186), 328
- Marko, L., 92(199), 101(177), 112(177), 131(167, 177), 143, 144
- Marks, T. J., 80(45), 82, 256(187), 258(187), 328
- Marsh, R. E., 244(16), 250
- Marzilli, L. G., 359(119), 360(118), 378(118), 379(118), 380(118, 119), 389(131(167, 177), 143, 144
- Marzilli, P. A., 359(119), 360(118), 378(118), 379(118), 380(118, 119), 389(119), 390(118), 444
- Masada, H., 130(222, 224), 131(223), 145
- Mason, R., 36(50, 85), 64(50), 65(50), 66(50), 67(50), 76(85), 77(85), 82, 83, 281(188), 282(6a), 323, 328, 344(120, 383(120), 444
- Masse, J. P., 308(84), 325
- Masters, C., 68(92, 93), 83
- Materikova, R. B., 149(110), 150(114), 151(113, 114), 152(112, 115, 116), 153(113, 115), 154(113, 117), 204
- Matsumoto, H., 15(63), 20
- Matsumoto, Y., 137(247), 145
- Matteson, D. S., 57(95), 64(94), 84
- Mawby, R. J., 56, 59(161), 85, 94(168), 95(92, 93, 108), 98, 99(168), 101(92), 102(92), 104(92, 93, 168), 107(169), 109(169), 114(169), 115(94), 116, 119(108), 120(108), 123(170), 125(168), 137(92, 94), 138(93), 142, 143, 367(70a), 443

- Mayle, C., 370(99), 393(99), 398(99), 413(99), 444
- Mays, M. J., 36(38, 39), 59(13, 14, 15, 16, 17), 69(68), 70(68), 77, 79(68), 81, 82, 83, 84, 289(21), 324, 342(121), 350(121), 360(121), 383(121, 122), 394(121, 122), 396(121, 122), 444
- Medema, D., 138(173), 143
- Meier, M., 69(98), 84
- Meister, H., 149, 204
- Melnikov, V. N., 246(64), 251
- Melville, D. P., 60, 82
- Meneus, F., 150(37), 202
- Menzies, E. M., 147, 202
- Menzies, R. C., 147, 148(104), 173(104), 204
- Mérour, J.-Y., 120(23), 128(23), 140
- Mervyn, L., 356(97), 384(97), 385(97), 406(167), 444, 446
- Merz, E., 246(57), 251
- Messerschmidt, R., 358(66), 430(66), 443
- Mestroni, E., 334(123), 348(123), 350(42), 366(42), 367(42), 387(42), 390(42), 432(42), 442, 444
- Mestroni, G., 133(76, 77), 141, 334(123), 342(38, 39, 43, 47, 49), 345(16, 40, 43, 47, 49, 83), 346(16), 347(16), 348(123), 350(47, 48, 83), 351(40, 42, 43, 45), 354(16), 355(40, 43), 356(16, 46), 357(43), 361(16, 37, 45), 366(39, 42), 367(42, 46, 48), 372(16, 44), 375(40, 49), 376(40, 44, 49, 83), 377(37, 43, 47), 378(16, 37, 43, 47), 379(16, 37, 38, 43, 44), 380(16, 44), 381(44), 386(43), 387(42, 46), 388(16, 40, 43, 46), 389(40, 43), 390(41, 42, 46, 47, 49), 391(16), 392(40, 43, 47), 393(38, 44), 397(83), 405(37, 44), 407(41, 47), 413(41), 414(45), 417(47, 49), 421(41), 424(41), 429(44), 432(42, 45, 49), 441, 442, 443, 444
- Midland, M. M., 15(54), 20
- Miller, J., 36(11), 45(99), 46(99), 61(99), 65(11), 66(11), 67(11), 68(11), 81, 84
- Miller, J. M., 219(58), 251
- Mills, O. S., 60(71), 83, 231(28), 250
- Miltenberger, K., 156(146), 205
- Minghetti, G., 39(100), 45(100), 46(25, 27), 50(23), 58(26), 68(6), 74(25), 75(25), 76(27), 79(27), 80(25, 100), 81(100), 81, 82, 84
- Mingos, D. P. M., 318(188a), 328
- Minichelli, D., 344(27), 442
- Mitchard, L. C., 128(101), 130(101), 142
- Mitchell, C. M., 257(168), 273(168), 328
- Mitsudo, T., 130(224), 145
- Mizuta, T., 360(125), 383(125), 396(125), 437(124), 444, 445
- Moerikofer, A. W., 13(40), 19
- Moerler, H. D., 69(105), 84
- Mole, T., 129(102), 142
- Monaro, S., 209(3), 210(3), 249
- Monerjan, A., 149(7), 202
- Morallee, K. G., 345(82, 83), 350(83), 371(81a), 376(82, 83), 377(82), 397(83), 443
- Mori, Y., 129(229), 145
- Moris, D., 123(170), 143
- Moritani, I., 8(15, 16), 19
- Morozov, N. G., 310(4a), 323
- Morris, D. E., 95(174), 143
- Morrison, D. L., 257(189), 258(189), 328
- Mortenson, R. A., 208(59), 251
- Mosa, D. N., 433(12), 438(12), 441
- Mowat, W., 118(243), 122(243), 136(42), 140, 145, 310(239), 311(189a, 239), 312(144, 145, 189a, 239), 314(144, 145, 189a, 239), 315(189a), 316(144, 145, 239), 318(189a), 319(144, 145, 189a, 239), 321(189a), 322(189a), 327, 328, 330
- Mrowca, J. J., 94(203), 144, 151(62, 105), 154(62), 203, 204
- Mühlofer, E., 256(4), 264(4), 283(4), 291(4), 323
- Mueller, F. J., 53, 61(142), 83, 85
- Müller, G., 414(126), 445
- Müller, H., 15(50), 19
- Müller, O., 414(126), 445
- Müller, J., 57(101), 84, 155(106), 204
- Müller, R., 244(84), 251
- Muggleton, P. W., 406(167), 446
- Muir, K. W., 43(73), 83, 268(46), 281(184, 190, 191), 282(184, 190, 191), 283(184, 191), 305(191), 312(74), 313(74), 316(74), 317(74), 320(74), 324, 325, 328
- Mukhedkar, A. J., 138(175), 139(176), 143

Muller, J.-C., 174(107), 204
 Murakami, M., 399(127), 445
 Murase, I., 48(129), 84
 Murin, A. N., 236(60), 251
 Murphy, W. S., 15(55), 20
 Murray, K. J., 15(50, 51), 19
 Murray, K. S., 378(53, 128), 430(53, 128),
 443, 445
 Muschi, J., 123(129), 142

N

Nagy, F., 434, 436, 446
 Nagy-Magos, Z., 101(177), 112(177), 131
 (177), 144
 Nakamoto, A., 71(67), 83
 Nakamura, A., 31(108), 66(102), 70(107),
 71(102, 106, 107), 74(107, 108), 84
 Nakamura, Y., 51(135), 85
 Nakano, T., 195(163), 206
 Narayan, S. R., 218, 226(61), 239(61),
 241(61), 251
 Nardin, G., 344(21, 22, 23, 24, 27), 347(21,
 24), 348(23), 402(28, 29), 442
 Nast, R., 69(104), 80(103), 84
 Nasta, M. A., 256(191a), 261(192, 192a),
 264(192), 274(191a), 296(192, 192a),
 328
 Nath, A., 220, 251
 Naumberg, M., 353(129), 357, 358(129), 370
 (129), 371(129), 373(129), 388(129),
 392(129), 411(129), 417(129), 445
 Nefedov, V. D., 234, 236(60, 63), 246(64),
 251
 Negishi, E., 16(64, 65), 20
 Negoescu, I., 230(20), 250
 Nelson, K. L., 9(18), 19
 Nelson, L. E., 298(23), 301(23), 324
 Neri, C., 344(30), 348(30), 378(30), 442
 Nerlekar, P. G., 298(25), 299(25), 324
 Nesmeyanov, A. N., 111(189), 121(189),
 122(178, 179, 180, 181, 182, 184),
 125(184), 126(181, 182, 183, 184),
 129(185, 186, 187, 188, 190), 144,
 148(111), 149(110), 150(114), 151(113,
 114), 152(112, 115, 116), 153(108, 109,
 113, 115), 154(113, 117), 204, 256(193,
 194), 286(154, 193), 327, 328
 Neubauer, D., 118(32), 138(32), 140

Neuffer, J., 152(22), 202
 Newlands, M. J., 290(146), 327
 Nicholson, B. K., 255(195), 328
 Nicolini, M., 34(49), 39(49), 74(49), 75
 (47), 82
 Nishido, T., 137(247), 145
 Noack, K., 89(191), 94(54), 107(54), 108
 (192), 112(191), 113(191, 192), 114,
 116, 122(54, 55, 193), 123(53, 54),
 125(54, 191, 192), 141, 144, 268(45),
 272(45), 324
 Nógrádi, M., 190(118), 205
 Noll, W., 298(196), 328
 Nordmeyer, J. P., 358(65), 443
 Nowat, M., 216(66), 218, 222, 246, 251
 Noyce, D. S., 192(119), 205
 Nozaki, H., 182(140), 205
 Nyholm, R. S., 282(179), 328
 Nyman, C. J., 134(11), 139

O

Oberkirch, W., 334(178), 336(178), 446
 O'Brien, R. J., 262(168, 110, 183), 264
 (183), 290(110), 296(183), 325, 326,
 328
 Ochiai, E., 346(131), 350(131), 365(130,
 131), 376(131), 387(130), 388(130,
 131), 405(131), 406(131), 414(131),
 445
 Ochiai, M., 172(156), 206
 Ogilvie, J. F., 122(194), 144
 Ogino, K., 258(196a), 289(196a), 328
 Ohgo, Y., 434(132), 437(133), 438(133),
 445
 Ohno, K., 134(195, 230, 231), 138(232),
 144, 145, 299(128), 308(128), 309
 (128), 327
 Okada, A., 265(214), 329
 Okawara, R., 148(73, 172), 155(73), 156
 (73), 157(73), 160(73, 74, 75), 174
 (74, 75, 76), 175(75), 203, 206
 Okhlobystin, O. Y., 149(120), 155(120), 205
 Okinoshima, H., 308(240a), 330
 Okumura, Y., 48(120), 84
 Oldenzien, O. H., 193(94), 194(94), 204
 Oliver, A. J., 29(84a), 83, 124(197), 135
 (196), 137(198), 144, 258(196b), 259
 (196b), 329

Oliver, J. D., 73(43), 74(43), 82
 Ollis, W. D., 189, 205
 Oppenheimer, E., 134(34), 140
 Orchin, M., 118(198a), 131(153), 143, 144
 Orenski, P. J., 310(25a), 324
 Orlova, L. V., 127(249, 250), 145
 Ormand, K. L., 189(121, 122, 123), 205
 Osborn, J. A., 134(9, 10), 135(10, 89), 139, 141, 258(60), 299(60), 304(60, 197), 305(60, 197), 309(60), 325, 329
 Otsuka, S., 31, 66(102), 69(110), 70, 71(67, 102, 106, 109, 110), 72(52, 110), 73, 74(107, 108, 110), 75(111), 82, 83, 84
 Ouellette, R. J., 161(124), 174(124, 127), 180(124), 182(125, 126, 127, 144), 205
 Overman, R. F., 234(22), 250

P

Padoa, G., 58(89), 83
 Pailles, W. H., 404(134), 445
 Palagyi, J., 92(199), 144
 Palazzi, A., 95(233), 135(233), 145
 Panattoni, C., 150(37), 202
 Pande, K. C., 173(128), 180(128), 205
 Pańkowski, M., 115(200), 130(200), 144
 Pannell, K. H., 29(83), 83, 128(151, 201), 129(149, 201), 143, 144, 153(65), 203, 256(163, 164, 199), 263(164), 272(163, 199), 287(163), 288(164), 312(164, 198, 199), 319(164), 321(164, 199), 327, 329
 Panov, E. M., 169(85, 129), 174(85), 204, 205
 Parish, R. V., 258(5, 135), 268(135), 271(135), 272(135), 273(135), 275(135), 277(135), 280(135), 289(5), 291(5), 294(248), 299(5, 135), 304(135), 305(135), 307(5), 318(248), 323, 325, 327, 330
 Parker, W., 247(19), 250
 Parkins, A. W., 315(145a), 327
 Parrott, J. C., 155(30), 164(30), 202
 Parry, D. J., 258(135), 268(135), 271(135), 272(135), 273(135), 275(135), 277(135), 280(135), 299(135), 304(135), 305(135), 327
 Parshall, G. W., 90(202), 94(203), 144, 269(200), 329

Partis, R. A., 61(2a), 81
 Patil, H. R. H., 256(201), 264(201), 268(201), 329
 Patmore, D. J., 258(25b), 259(25b), 290(202), 324, 329
 Paul, I., 255(94), 256(94), 257(95), 258(95), 262(96), 286(97), 326
 Paulik, F. E., 118(203a), 144
 Pauson, P. L., 28(112), 37(70), 54, 55(70), 60(70, 71), 83, 84, 93(134), 125(134), 130(64), 141, 142, 231(28), 250
 Pearce, R., 311(77, 176a), 314(77, 176a), 315(77, 145a, 176a), 319(77), 320(77), 321(77), 322(77), 325, 327, 328
 Pearson, R. G., 55(69), 56(69), 69(98), 83, 84, 94(48, 168), 97(48), 98(168), 99(168), 100(48), 104(48, 168), 107(169), 109(169), 114(169), 120(148), 125(168), 127(48), 140, 143, 161, 162(131), 205
 Pelekhov, V. I., 209(3), 210(3), 249
 Pélichet, C., 131(163), 143
 Pellizer, G., 133(76, 77), 141, 342(43), 345(16, 43, 82, 83), 346(16), 347(16), 350(83), 351(43, 45), 354(16), 355(43), 356(16), 357(43), 361(16, 45), 366(16), 372(16, 44), 375(44), 376(82, 83), 377(43, 82), 378(16, 43), 379(16, 43, 44), 380(16, 44), 381(44), 386(43), 388(16, 43), 389, 391(16), 392(43), 393(44), 397(83), 405(44), 414(45), 429(44), 432(45), 442, 443
 Perego, G., 344(30), 348(30), 378(30), 442
 Perrotti, E., 344(30), 348(30), 442
 Petrovskii, P. V., 150(114), 151(114), 204
 Phelan, P. F., 359(144), 369(144), 374(144), 389(144), 445
 Pickholtz, Y., 137(33a), 140
 Pidcock, A., 286(136), 287(136), 308(101), 326, 327
 Piesbergen, U., 150(36), 202
 Pietropaola, R., 254(243), 330
 Pietrusza, E. W., 298(225), 329
 Pignataro, S., 53(53, 72), 82, 83
 Pinnock, H. A., 364(33, 34), 386(33), 388(33, 34), 390(33), 408(33), 411(33), 412(33), 415(33), 442
 Piper, T. S., 231(68), 251, 254(203), 256(203), 263, 301(203), 329

Pitcher, E., 122(226), 145
 Poblath, H., 254(139), 327
 Poddar, S. N., 402(135), 445
 Podoa, G., 58(113), 84
 Poe, M., 348(20), 384(20), 442
 Poë, A. J., 92(104), 142
 Pohlmann, J. L. W., 155(132), 205
 Poilblanc, R., 95(204), 119(56), 121(56), 141, 144
 Pollman, T. G., 109(19a), 118(19b), 121(19a), 140
 Polovyanyuk, I. V., 129(185, 186, 188, 190), 144
 Pomeroy, R. K., 289(203a, 203b), 329
 Pospelova, T. A., 353(142), 368(142), 369(142), 371(142), 372(142), 373(142), 445
 Postgate, J. R., 53(79), 83
 Powell, H. M., 59(162), 85
 Powell, K. G., 135(205), 144
 Prater, B. E., 59(13, 14, 15, 16, 17), 60(114, 115, 116), 81, 82, 84, 289(21), 324
 Pratt, D. W., 64(81), 83
 Pratt, J. M., 133(40), 140, 332(85, 86), 336(17, 136, 137), 338(136), 341(86, 87), 342(85, 86, 136, 139), 345(17), 346(61, 136), 348(35, 88, 136), 349(136, 139), 350(6, 78), 351(6, 136), 358(136, 140), 361(139), 362(136), 364(136), 378, 380(17), 384(35, 88, 136), 385(136), 393(77), 398(77), 403(136), 404(140), 407(136), 408(136), 413(61, 62, 77, 136), 414(77), 417(61), 419(136), 420(61, 78, 139), 421(136), 422(84), 423(84, 138), 424(84, 136), 425(136), 427(3, 136), 430(63), 432(136), 434(6, 141), 441(136), 441, 442, 443, 444, 445
 Preobrazhenskii, H. A., 373(183), 419(183), 446
 Preuss, F. R., 169(133), 205
 Price, M. G., 364(54), 365(54), 387(54), 443
 Price, M. J., 177(83), 181(83), 183(83), 203
 Price, S. J. W., 156(57), 203
 Prokai, B., 90, 143
 Pucheault, J., 174(107), 204
 Puddephatt, R. J., 89(67), 137(66), 138(66), 141

Pukhnarevich, V. B., 310(203c, 233a), 329, 330
 Puppis, M., 342(64), 345(64), 377(64), 378(64), 386(64), 390(64), 392(64), 425(64), 427(64), 432(64), 443
 Puri, S. P., 59(91), 83
 Puxeddu, A., 345(16), 346(16), 347(16), 354(16), 356(16), 361(16), 366(16, 50), 367(50), 372(16), 376(50), 377(50), 378(16, 50), 379(16, 50), 380(16), 388(16), 391(16, 50), 433(51), 441, 443

R

Rad'kova, O. M., 310(4a), 323
 Rafaeloff, R., 247(73), 251
 Randaccio, L., 344(21, 22, 23, 24, 27), 347(21, 24), 348(23), 402(28, 29), 442
 Randall, G. L. P., 133(40), 140, 336(17), 345(17), 378(17), 380(17), 442
 Rao, K. A., 220(62), 251
 Rathke, M. W., 15(52, 61, 63), 19, 20
 Ratusky, J., 247(53), 251
 Rausch, M. D., 122(207), 137(206), 144
 Ravindranathan, T., 155(23), 202
 Ray, F. E., 7(9), 19
 Razuvaev, G. A., 254(234), 255(234), 330
 Redman, B. T., 189(123), 205
 Reed, H., 289(102), 326
 Rei, M.-H., 178(12), 202
 Reichard, D., 93(227), 129(227), 145, 330
 Reichold, P., 224, 225, 228, 236(9), 237(9, 10, 11), 245(9, 11), 250, 251
 Reich-Rohrwig, P., 117(208), 144
 Reikhsfel'd, V. O., 299(204), 301(204), 329
 Reis, H., 118(32), 138(32), 140
 Reisenhofer, E., 345(16), 346(16), 347(16), 354(16), 356(16), 361(16), 366(16, 50), 367(50), 372(16), 376(50), 377(50), 378(16, 50), 379(16, 50), 380(16), 388(16), 391(16, 50), 441, 443
 Repe, B. C. L., 164(32), 202
 Rest, A. J., 105(209), 122(209), 144, 239(70), 251
 Reutov, O. A., 158(134), 205
 Reynolds, L. T., 149(25), 150, 151(25, 135), 152(25), 202, 205
 Rhee, I., 61(59), 83

Rhodes, S. P., 15(58), 16(58), 20
 Richards, O. V., 172(18), 202
 Richards, R. L., 42(8, 9), 45(8), 46(8, 9),
 53(79), 60, 80(8, 9), 81, 82, 83
 Richer, J.-C., 183(38), 202
 Richter, J. W., 216(94), 252
 Ridsdale, S. C., 422(84), 423(84), 424(84),
 427(3), 441, 443
 Riedel, H. J., 246(57), 251
 Risen, W. M., 289(235), 330
 Roberts, R. D., 189(123), 205
 Roberts, R. M., 182(170), 206
 Robertson, C. G., 51(22), 82
 Robertson, G. B., 125(24), 140
 Robey, R. L., 165(153), 193(94), 194(94),
 200(157), 201(158), 204, 205, 206
 Robiette, A. G., 281(205), 286(205), 329
 Robinson, W. T., 258(206), 281(109), 282
 (109), 283(206), 326, 329
 Rochow, E. G., 155(136), 205
 Rodrigo, R., 432(57), 443
 Rogič, M. M., 15(52, 61, 62, 63), 19, 20
 Rohwedder, W. K., 438(117), 444
 Roper, W. R., 61(37), 67(37), 82, 136(72),
 141, 268(81), 269(81), 325
 Rose, N. J., 387(25), 442
 Rosenblum, M., 152(137), 205
 Rosenthal, A., 132(210), 144
 Roschupkina, O. S., 353(142), 368(142),
 369(142), 371(142), 372(142), 373
 (142), 445
 Ross, E. P., 255(103), 277(103, 207), 326, 329
 Ross, R., 223(72), 246(72), 251
 Rouschias, G., 43(117), 80(117), 84
 Roustan, J.-L., 120(23), 128(23), 140
 Ruch, M., 108(192), 113(192), 125(192), 144
 Rudakova, I. N., 373(183), 419(183), 446
 Rudakova, I. P., 353(142), 368(142),
 369(142), 371(142), 372(142), 373(18,
 142), 374(18), 442, 445
 Ruddick, J. D., 139(211, 212, 213), 144,
 145, 311(238), 312(238), 313(238), 314,
 (238), 315(238), 317(238), 330
 Rudler, H., 53(157), 85
 Rupilius, W., 118(198a), 144
 Rush, J. E., 409, 414(91a), 415(91a), 444
 Russell, D. R., 344(120), 383(120), 444
 Russo, P. J., 255(124), 264(124), 273(124),
 275(124), 280(124), 288(124), 326

Ryan, J. W., 298(208), 329
 Ryang, M., 61(59), 83
 Rylander, P. N., 308(209), 329
 Ryukhin, Y. A., 246(64), 251

S

Saalfeld, F. E., 257(117), 258(116, 117,
 210), 261(192, 192a), 271(116, 117),
 287(210, 211), 288(210, 211, 212, 213),
 289(30, 212), 296(192a), 324, 326, 328,
 329
 Sacco, A., 58(89), 83
 Saegusa, T., 22, 47(124), 48(118, 119, 120,
 123, 124, 128, 129, 132), 49(119a, 121,
 125, 126, 130, 131), 61(127), 80(124,
 132), 84, 85
 Sakriker, S., 371(69), 372(69), 398(69),
 410(69), 415(69), 443
 Sakurai, H., 265(214), 329
 Sakurai, T., 350(143), 367(143), 445
 Sanderson, R. T., 4(4), 18
 Sarapu, A., 26(133), 55(133), 85
 Sarkar, P. B., 57(134), 85
 Sarkar, S., 57(134), 85
 Sato, M., 51, 85
 Schaerer, U., 122(193), 144
 Schempff, R., 169(28), 170(28), 202
 Schiavelli, M. D., 192(119), 205
 Schindler, H. D., 57, 82
 Schlesinger, H. I., 3(3), 4(4, 5), 5(7), 18
 Schlessinger, G., 53(138), 85
 Schmid, G., 260(215), 262(215), 268(215),
 293(215), 329
 Schmidbaur, H., 314(221), 315(221), 329
 Schmidt, E., 128(45, 46), 140
 Schneider, M. L., 259(216), 267(216), 329
 Schneider, P. W., 359(144), 369(144),
 374(144), 389(144), 445
 Schneider, R., 150(40), 203
 Schneider, R. J. J., 57(56), 80(56), 83
 Schön, A., 237(13), 245(12, 13), 250
 Schott, M., 268(236), 330
 Schrauzer, G. N., 53(138), 63, 85, 258
 (216a), 267(216a), 329, 336(145), 346
 (161), 351(149, 161), 352(149), 353,
 354(147), 355(148, 149), 356(149),
 357, 358(158), 360(161, 163), 365
 (117a, 158), 366(147, 158), 367(146,

- 147, 154, 161, 164), 368(146, 147, 151, 154, 158, 161, 164), 369(147, 151, 160, 161, 163), 370(146, 147, 151, 154, 161, 162, 163), 371(147, 154, 155, 159, 161, 162, 163), 372(147, 151, 154, 155, 162, 163), 373(147, 155, 163, 164), 374(147, 154, 158), 375(147, 154, 155, 158, 161), 377(158), 378(147, 155, 158), 381(158), 387(161), 388(147, 151, 153, 154, 155, 161, 162, 163, 164), 389(163, 165), 390(146, 151, 161), 391(161), 392(146, 161, 163), 393(161), 396(163), 397(161), 398(163), 400, 405(154, 158), 406(158, 163), 407(159), 408(162), 410(161), 411(155, 162), 412(155, 162), 413(159, 163), 414(162, 163), 415(155, 159, 162, 163), 416(159, 163), 417(147, 154, 163), 418(154, 163), 419(155, 162), 420(155, 159), 421(154, 155, 159), 422(160), 423(160), 426(161, 164), 427(157, 161), 429(163), 432(156, 157, 161, 163, 164), 433(161, 163), 437(164, 165), 438(159), 439(150), 444, 445, 446
- Schrieke, R. R., 255(217, 218), 256(217, 218), 258(217), 272(217, 218), 277(217), 278(218), 279(218), 286(217, 218), 287(217, 218), 329
- Schulz, H., 69(104, 105), 84
- Schuster-Woldan, H. G., 100(214), 145
- Schwartz, A., 247(73), 251
- Scott, J. L., 59(78), 60(78), 83
- Seaborg, G. T., 246, 251
- Sears, Jr., C. T., 99(132), 137(71), 141, 143
- Seck, J. A., 439(150), 445
- See, E. G., 155(82), 203
- Seeholzer, J., 225(15), 241(15), 250
- Seifert, F., 156(146), 205
- Selin, T. G., 301(219), 329
- Selke, E., 438(117), 444
- Semion, V. A., 91(6), 139
- Semmlinger, W., 151(21), 202
- Seyam, A. M., 256(187), 258(187), 328
- Seyferth, D., 329
- Seyler, J. K., 333, 342(109), 359(108), 381(108, 109, 110, 111), 382(108, 109, 110), 383(108), 394(108), 395(107, 109), 399, 400(109), 409, 410(109), 413(110), 414(109, 110), 416(108), 425(109), 428, 430(111), 432(109), 434(107, 108), 435(107, 109), 436(106, 108, 109), 437(108), 438(107), 444
- Shakshooki, S. K., 73(60), 83
- Sharp, R. L., 14(46), 19
- Shaw, B. L., 43(117), 60(71), 68(92, 93), 80(117), 83, 84, 135(84), 136(7, 215), 137(63, 85, 86), 139(211, 212, 213), 139, 141, 144, 145, 269(245), 289(102), 325, 326, 330, 342(31), 442
- Shaw, B. W., 83
- Shaw, D. L., 182(125, 126), 205
- Shaw, N., 356(97), 384(97), 385(97), 406(167), 444, 446
- Shearer, H. M. M., 259(216), 267(216), 329
- Sheinker, Y. N., 149(110), 204
- Sheldrick, G. M., 155(82), 156(138), 203, 205, 281(205), 282(106), 286(205), 296(106), 326, 329
- Sheldrick, W. S., 156(138), 205
- Sheline, R. K., 69, 83
- Shepherd, W. A., 81(158), 85
- Sheridan, J., 150(160), 206
- Shibano, T., 299(229), 306(229), 308(229), 310(229a), 330
- Shibata, S., 150, 205
- Shikata, E., 223(36), 250
- Shimizu, S., 414(180), 420(67, 180), 425(180), 426(67), 443, 446
- Shimizu, T., 61(127), 84
- Shinra, K., 370(181), 371(181), 430, 446
- Shiotani, A., 314(221), 315(221), 329
- Shirafuji, T., 182(140), 205
- Shono, T., 370(181), 371(181), 430, 446
- Shortland, A., 118(243), 122(243), 145, 310(239), 311(189a, 239), 312(144, 189a, 239), 314(144, 189a, 239), 315(189a), 316(144, 239), 318(189a), 319(144, 189a, 239), 321(189a), 322(189a), 327, 328, 330
- Shubkin, R. L., 93(227), 129(227), 145, 330
- Shurawlev, M. A., 236(63), 251
- Sibert, J. W., 358(158), 365(117a, 158), 366(158), 367(154), 368(154, 158), 369(154, 158), 370(154), 371(154, 155), 372(154, 155), 373(155), 374(154, 158), 375(154, 155, 158), 377(158), 378(155, 158), 381(158), 388(154, 155), 405(154, 158), 406(158), 411(155), 412(155), 415(155), 417(154), 418(154), 419(155),

- 420(155), 421(154, 155), 427(157), 432
(156, 157), 444, 445
- Sidgwick, N. V., 192(141), 205
- Siegl, W. O., 130(215a), 145
- Siekierska, K. E., 221, 222(75), 243, 245
(76), 251
- Sim, G. A., 42(8), 45(8), 46(8), 81
- Simandi, L., 434, 436, 446
- Simons, P. B., 255(153), 256(153), 286
(153), 287(153), 327
- Simpson, J., 255(195), 328
- Simpson, K. A., 261(26a), 291(26a), 324
- Simpson, R. N. F., 281(205), 286(205), 329
- Singleton, E., 136(7, 215), 139, 145
- Siuda, A., 221(75), 222(75), 243(75), 251
- Skapski, A. C., 282(222), 312(144, 145), 314
(144, 145), 316(144, 145), 319(144,
145), 327, 329
- Skripkin, V. V., 256(194), 328
- Slade, R. M., 269(245), 330
- Slater, J. H., 59(65), 83
- Sleezer, P. D., 185(142), 205
- Smith, C. A., 259(133), 268(133), 269(132,
133), 301(132, 133), 303(132), 304(132,
133), 305(132), 327
- Smith, D. L., 57, 85
- Smith, E. L., 356(97), 384(97), 385(97),
406(167), 426(72), 443, 444, 446
- Smith, J. G., 255(94), 256(94), 257(95),
258(95), 326
- Smith, M. J., 128(103), 142
- Smith, N. O., 59(162), 85
- Smith, S. A., 105(160), 109(160), 110(160),
136(160), 143
- Snell, A. H., 234, 251
- Snyder, C. H., 15(57), 20
- Sokolovskii, L. L., 209(3), 210(3), 249
- Sokolowska, A., 221, 243(76), 245(76), 251
- Solomon, T. W., 109(19a), 121(19a), 140
- Sommer, L. H., 257(223), 258(223), 298,
299(224), 301(224), 304(223), 308
(67, 223, 224), 325, 329
- South, Jr., A., 182(125, 126, 143, 144), 205
- Spalding, T. R., 278(49), 285(49), 287
(226), 288(49), 324, 329
- Spano, H., 216(79), 251
- Speier, G., 256(177), 262(177), 268(177),
269(177), 293(177), 294(177), 296
(177), 328
- Speier, J. L., 298(208), 329
- Spencer, D. D., 289(227), 329
- Spencer, M. S., 435(168), 446
- Sperati, C. R., 346(131), 350(131), 365
(131), 376(131), 388(131), 405(131),
406(131), 414(131), 445
- Srinivasan, S. C., 218(44, 81), 226(44),
229(42, 44, 45), 230(44, 80), 231, 232
(42), 233(42), 238(44), 240(44, 45),
241(80), 243(44), 248(42, 45), 250, 251
- Stafford, S. L., 130(152), 143
- Stallick, J. K., 72(139), 85
- Starke, K., 216(82, 83), 251
- Starysh, M. P., 63(1, 2), 74(1, 2), 81
- Steele, D. F., 95(216), 133(216), 145
- Stefani, L., 342(47, 49), 345(16, 47, 49), 346
(16), 347(16), 350(47), 354(16), 356(16),
361(16), 366(16), 372(16), 375(49),
376(49), 377(47), 378(16, 47), 379
(16), 380(16), 388(16), 390(47, 49),
391(16), 392(47), 407(47), 417(47, 49),
432(49), 441, 442
- Steinrücke, E., 334(178), 336(178), 446
- Stenson, J. P., 37(140, 143, 146), 38(146),
40, 41(140), 44(146), 51(148), 57(146,
148), 61(140, 143, 146, 148), 79(143),
85
- Stephany, R. W., 80(141), 85
- Stephenson, T. A., 95(216), 133(216), 145
- Stern, H., 256(4), 264(4), 283(4), 291(4),
323
- Sternberg, H., 289(186), 328
- Stewart, R. P., 122(217), 124(217), 126
(217), 131(217), 145
- Stich, H., 133(164), 143
- Stille, J. K., 117(131a, 218), 138(131a, 218),
142, 145
- Stobart, S. R., 254(115a), 326
- Stock, A., 3(1), 5, 18
- Stock, L. M., 9(19), 19
- Stone, F. G. A., 73, 74(43), 82, 83, 91(238),
122(44, 135, 226), 125(133, 135), 126
(33, 44), 130(152), 137(5), 138(175),
139(176), 139, 140, 142, 143, 145, 254
(1, 228), 255(94), 256(35, 94), 257(6, 35,
95, 168, 169, 170), 258(95), 262(39, 96),
266(169, 170), 267(169), 269(169), 272
(6, 169), 273(6, 168, 169, 170), 276
(6), 278(169), 283(1, 6), 286(97), 288

- (35, 169), 292(39), 300(1), 323, 324, 326, 328, 329
- Stranks, D. R., 174(144a), 205
- Stratton, P., 59(21), 82
- Streitwieser, Jr., A., 175(145), 205
- Strohmeier, W., 53(63), 61(142), 83, 85, 156(146), 205, 244(84), 251
- Struchkov, Yu. T., 91(6), 139
- Stubbs, W. H., 28(112), 37(70), 54, 55(70), 60(70, 71), 83, 84, 93(134), 125(134), 142
- Su, S. R., 93(219), 109(219), 128(219), 129(219, 220), 145
- Stubba Rao, B. C., 11(29, 31), 13(37), 19
- Sujishi, S., 8(11), 19
- Sumida, S., 137(247), 145
- Sushchinskaya, S. P., 310(203c, 233a), 329, 330
- Susuki, T., 120(221), 129(221), 145
- Sutherland, I. O., 189(121, 122, 123), 205
- Sutin, N., 208, 216, 221, 223, 224(40), 238(56), 240(85), 246, 247(85), 250, 251
- Suzuki, A., 15(63), 20
- Suzuki, K., 399(127), 445
- Suzuki, T., 360(125), 383(125), 396(125), 435(170), 436(171), 438(172, 173), 445, 446
- Svoboda, P., 310(45a), 324
- Swaddle, T. W., 65(28), 82
- Swallow, A. J., 174(17), 202
- Swann, B. P., 190(95), 191(95, 96), 193(94), 194(94), 199(97), 204
- Swanwick, M. G., 128(101), 130(101), 142
- Swenson, C. A., 409, 414(91a), 415(91a), 444
- Swinden, G., 367(70a), 443
- Swisher, J. V., 298(23), 301(23), 324
- Szabo, P., 131(167), 143
- Szilard, L., 207, 211, 251
- T**
- Takahashi, H., 35(74), 74(74), 83
- Takahashi, S., 299(178, 229), 306(229), 308(229), 310(178, 229a), 328, 330
- Takeda, N., 48(123), 84
- Takegami, Y., 130(222, 224), 131(223), 145
- Takeuchi, K., 10(23, 24), 19
- Takeuchi, S., 434(132), 437(133), 438(133), 445
- Tamao, K., 259(167), 328
- Tanaka, K., 334(178), 336(178), 446
- Tanezawa, K., 49(131), 84
- Tatsuno, Y., 66(102), 69(110), 70(107, 110), 71(67, 102, 107, 109, 110), 72(52, 110), 73(110), 74(107, 110), 75(111), 82, 83, 84
- Taube, M., 342(174), 346(174), 364(174), 387(174), 425(174), 446
- Tauzher, G., 342(49), 345(16, 49), 346(16), 347(16), 350(48), 351(45), 354(16), 356(16), 361(16, 45), 366(16, 48), 367(48), 372(16), 375(49), 376(49), 378(16), 379(16), 380(16), 388(16), 390(49), 391(16), 414(45), 417(49), 432(45, 49), 433(51), 441, 442, 443
- Taylor, E. C., 148(86, 154, 155), 149(87, 88), 157(90), 158(147, 149), 159(147, 152), 163(89), 164(90, 91), 165(153), 169(147), 170(150), 171(91, 152), 172(147, 156), 177(92), 178(92), 187(92), 190(95), 191(95, 96), 192(148), 193(94), 194(94), 196(93), 199(97), 200(147), 201(158), 202(151), 204, 205, 206
- Tengler, H., 122(22), 140
- Terashima, S., 155(23), 202
- Thomas, F. G., 234(21), 250
- Thomas, V. G., 220(62), 251
- Thompson, J. A. J., 255(153), 256(153), 258(121), 286(153), 287(153), 326, 327
- Thorp, R. G., 342(139), 346(61), 349(139), 413(61, 62), 417(61), 420(61, 139), 430(63), 443, 445
- Thorsteinson, E. M., 123(170), 143
- Tinker, H. B., 95(174), 143
- Tobe, M. L., 346(100, 101), 357(102), 382(100, 101), 383(100, 101, 102), 393(101), 396(100, 101), 397(101, 102), 399(101, 102), 402(102), 406(100, 102), 410, 411, 414(100, 101, 102), 416(101, 102), 420(100, 102), 429(100, 102), 438(102), 444
- Tomasi, R. A., 265(112), 326
- Tomita, S., 48(132), 49(119a, 121, 125, 126, 130, 131), 80(132), 84, 85
- Toropova, A. V., 236(63), 251

Toropova, M. A., 246(64), 251
 Towl, A. D. C., 281(188), 328
 Trabał, J. E., 219(92), 226(92), 239(92), 252
 Traylor, T. G., 181(159), 206
 Treichel, P. M., 27(154), 32(144, 147), 33(144, 145), 34, 37(143, 147), 38(145, 146), 39(146), 40(147), 41(84, 149), 42(147), 44(146), 45(147), 46(147), 50(147), 51(148), 54(154), 55(154), 56(153, 154), 57(146, 148), 61(143, 146, 148), 68(147), 76(147), 77, 78, 79(84, 149, 150, 151, 153), 80(144, 147, 153), 83, 85, 93(227), 119(20), 120(20), 121(20), 122(217, 226), 124(217, 225), 126(217), 219(227), 130(152), 131(217), 140, 145, 330
 Triggs, C., 161(29), 162, 202
 Trofimov, B. A., 310(203c, 233a), 329, 330
 Troughton, P. G. H., 282(222), 329
 Truelock, M. M., 310(78), 311(76, 78), 312(74, 76, 78), 313(76, 78, 331), 314(76, 78, 231), 315(76, 78, 231), 316(74, 78, 231), 317(74), 319(78, 231), 320(74, 76, 78, 231), 231(78, 231), 322(78, 231), 325, 330
 Tsuji, J., 35(74), 74(74), 83, 118(228), 120(221), 129(221, 229), 134(195, 230, 231), 138(228, 232), 144, 145, 299(128), 308(128), 309(128), 327
 Tsutsumi, S., 61(59), 83
 Turnbull, A. G., 149(55), 203
 Tune, D. J., 259(105a), 326
 Turco, A., 268(37), 324
 Turner, J. J., 239, 251
 Turpin, C. L., 259(105a), 326
 Tyler, J. K., 150(160), 206

U

Uemura, S., 189(162), 191, 195(163), 199(162), 206
 Ugi, I., 22, 47(156), 85
 Ugo, R., 298(232), 330
 Uguagliatti, P., 66(29), 74(29), 82, 95(233), 135(87, 233), 141, 145, 254(243), 330
 Umeno, M., 299(173), 305(173), 308(173), 309(173), 328

Umetani, T., 414(180), 420(67, 180), 425(180), 426(67), 443, 446
 Unni, M. K., 14(44), 19
 Uramoto, Y., 310(240c), 330
 Urry, G., 260(237), 330
 Ustynyuk, N. A., 111(189), 121(189), 129(189), 144
 Ustynyuk, Y. A., 129(187), 144

V

Valenti, V., 59(55), 82
 Vamplew, D., 160(20), 202
 van Bekkum, H., 358(10), 434(10), 436(10), 438(10), 441
 van den Bergen, A., 351(174a), 358(174a), 376(174a), 377(174a), 378(174a), 393(174a), 427(174a), 446
 Vandenborn, H. W., 289(36), 324
 Van der Kelen, G. P., 286(99, 100), 326
 Vander Jagt, D. L., 10(26), 19
 van Helden, R., 138(173), 143
 van Reijen, L. L., 358(10), 434(10), 436(10), 438(10), 441
 Vanston, N., 393(77), 398(77), 413(77), 414(77), 443
 Vaska, L., 301(233), 330
 Vastine, F. D., 136(72), 141
 Vasudev, P., 230(20), 250
 Van Tamelen, E. E., 53(157), 85
 Vaughn, L. G., 81(158), 85
 Vavrejn, B., 247(53), 251
 Viček, A. A., 351(76), 443
 Vobecky, M., 234(65), 251
 Vogel, M., 128(45), 140
 Vohler, G., 342(81), 443
 Vohler, O., 131(131), 142
 Volger, H. C., 135(234), 138(235), 145
 Volkova, L. G., 370(175), 424(175), 446
 Vol'pin, M. E., 370(175), 424, 433(116), 437(116), 444, 446
 von Ammon, R., 81(159, 160), 85
 von Kutepow, N., 118(32), 138(32), 140
 Voronkov, M. G., 254(180), 298(180), 299(180), 310(203c, 233a), 328, 329, 330
 Vrieze, K., 135(234), 138(235), 145
 Vyazankin, N. S., 254(234), 255(234), 330

W

- Wade, K., 59(65), 83, 278(73), 318(73), 325
Wagner, F., 360, 386(176), 446
Wagner, K. P., 34, 56(153), 79(151, 153), 80(153), 85
Walborsky, H. M., 117(236), 134(236), 145
Walker, P. J. C., 56, 59(161), 85
Wallbridge, M. G. H., 36(85), 76(85), 77(85), 83
Walton, A., 256(12, 234a), 257(234a), 264(12), 274(12), 275(12), 279(12), 280(12), 286(12), 323, 330
Walton, D. R. M., 192(8), 202, 259(105a), 326
Wardle, R., 138(82), 141
Ware, M. J., 285(134), 327
Watanabe, Y., 130(222, 224), 131(223), 145
Watkins, S. F., 65(58), 83
Watt, J. A. C., 308(20), 324
Watt, R., 125(24, 25), 140
Watter, D., 334(178), 336(178), 446
Watters, K. L., 289(235), 330
Wayland, B. B., 289(30), 324
Weast, R. C., 172(166), 206
Webber, I. H., 226(88), 251
Weber, J. H., 356, 369(160), 371(159), 387(25), 400, 407(159), 410, 413(159), 415(159), 416(159), 420(159), 421(159), 422(160), 423(160), 438(159), 442, 445
Weckermann, B., 216(52), 251
Weiss, A. J., 223(36), 232(38), 240(37), 250
Wender, I., 389(186), 328
Wenger, A., 260(110a), 262(110a), 269(110a), 326
West, B. O., 255(217, 218), 256(217, 218), 258(217), 272(217, 218), 277(217), 278(218), 279(218), 286(217, 218), 287(217, 218), 329, 351(174a), 358(174a), 376(174a), 377(174a), 378(53, 128, 174a), 393(174a), 427(174a), 430(53, 128), 443, 445, 446
West, R., 301(219), 329
Westlake, D. J., 94(98), 97(98), 100, 101, 127(98), 128(98), 142, 257(43), 275(43), 324
Wexler, S., 212, 251
Wheeler, A. G., 282(6a), 323
Wheeler, O. H., 219(92), 223(90, 91), 226(92), 239(92), 247(90), 251, 252
Whimp, P. O., 125(24), 140, 282(6a), 323
White, D. A., 153(59), 203
White, R. M., 212, 246, 250
Whitcar, B. R. D., 358(140), 404(140), 445
Whitesides, G. M., 117(237), 128(237), 145, 431(177), 446
Whitmore, F. C., 298(225), 329
Wiberg, K. B., 196, 206
Wien, K., 216(52), 251
Wild, S. B., 285(38), 324
Wiles, D. R., 218(44, 47, 61, 81), 219(46, 92, 95), 224(51), 226(44, 46, 61, 92), 229(42, 44, 45), 230(20, 44, 47), 231(44, 96), 232(42, 48), 233(42), 238(44), 239(48, 50, 61, 92), 240(44, 45, 50), 241(61), 243(44), 244(93), 245(51), 248(42, 45), 249(51), 250, 251, 252
Wiley, P., 200(168), 202(168), 206
Wiley, R. H., 200(168), 202(168), 206
Wilford, J. B., 59(162), 85, 91(238), 145
Wilke, G., 36(31), 74(31), 82, 137(123a), 142, 268(236), 330, 334(178), 336(178), 446
Wilkins, E. M., 147(103), 204
Wilkinson, G., 95(88), 102(88), 118(172, 243), 119(172), 122(243), 133(241, 242), 134(9, 10, 11, 43, 242), 135(10, 88, 89), 136(42, 242), 139(12), 139, 140, 141, 143, 145, 151(135), 152(169), 164(26), 205, 206, 231(68), 251, 254(203), 256(203), 258(60), 263, 299(60), 301(87, 203), 304(60, 197), 305(60, 197), 309(60), 310(239), 311(189a, 238, 239), 312(144, 145, 189a, 238, 239), 313(238), 314(144, 145, 189a, 238, 239), 315(189a, 238), 316(144, 145, 239), 317(238), 318(189a), 319(144, 145, 189a, 238, 239), 321(189a), 322(189a), 325, 327, 328, 329, 330, 333(70), 341(70), 342(70, 121), 346(70), 350(121), 360(5, 70, 121), 381(70), 383(5, 121, 122), 394(121, 122), 395(70), 396(5, 70, 121, 122), 413(70), 441, 443, 444
Williams, A. G., 133(40), 140, 336(17), 345(17), 378(17), 380(17), 442

- Williams, D. H., 387(25), 442
 Williams, D. L., 263(185), 328
 Williams, F. R., 389(2), 422(84), 423(84), 424(2, 84), 427(2), 441, 443
 Williams, R. J. P., 332(85, 86), 341(86, 87), 342(85, 86), 346(61), 348(35, 88), 350(78), 384(35, 88), 389(2), 393(77), 398(77), 413(61, 62, 77), 414(77), 417(61), 420(61, 78), 422(84), 423(84), 424(2, 84), 427(2, 3), 430(63), 434(141), 441, 442, 443, 444, 445
 Williams, R. R., 216(94), 252
 Williams, S., 161(124), 174(124, 127), 180(124), 182(127), 205
 Wilmarth, W. K., 350(52, 73), 367(52), 368(52), 369(52), 443
 Wilson, P. W., 263(185), 328
 Windgassen, R. J., 346(161), 351(161), 353(148), 355(148), 356(163), 357, 358(158), 360(161, 163), 365(158), 366(158), 367(161, 164), 368(158, 161, 164), 369(158, 161, 163), 370(161, 162, 163), 371(161, 162, 163), 372(162, 163), 373(163, 164), 374(158), 375(158, 161), 377(158), 378(158), 381(158), 387(161), 388(161, 162, 163, 164), 389(163, 165), 390(161), 391(161), 392(161, 163), 393(161), 396(163), 397(161), 398(163), 405(158), 406(158, 163), 408(162), 410(161), 411(162), 412(162), 413(163), 414(162, 163), 415(162, 163), 416(163), 417(163), 418(163), 419(162), 426(161, 164), 427(161), 429(163), 432(161, 163, 164), 433(161, 163), 437(164, 165), 445, 446
 Winfield, M. E., 350(11), 441
 Winstein, S., 173(128), 177(3), 180(128), 181(3), 182(170), 202, 205, 206
 Wirkkala, R. A., 163, 202
 Wittle, J. K., 260(237), 330
 Woffenden, N. P., 92(35), 94(37), 102(37), 105(37), 107(37), 108(37), 124(35), 125(37), 140
 Wojcicki, A., 90(239), 91(28, 239), 93(28, 219), 100(28), 101(239), 109(219), 111(1, 2, 2a), 116(2), 117(208), 121(1), 126(1, 2), 127(28), 128(28, 219), 129(219, 220), 139, 140, 144, 145, 324, 431(179), 446
 Wolf, G. K., 226(34), 228, 245, 246(34), 250
 Wolf, W., 171, 206
 Wong, L. Y., 346(100, 101), 357(102), 382(100, 101), 383(100, 101, 102), 393(101), 396(100, 101), 397(101, 102), 399(101, 102), 402(102), 406(100, 102), 410, 411, 414(100, 101, 102), 416(101, 102), 420(100, 102), 429(100, 102), 438(102), 444
 Wong, W. H., 219(95), 244(93), 252
 Wood, D. C., 94(97), 97(97), 113(99), 123(99), 125(97), 142
 Wood, J. M., 365(117a), 444
 Woods, D. D., 426, 443
 Woodward, P., 65(58), 83, 292(246), 330
 Work, S. D., 298(25), 299(25), 324
 Wozniak, B., 311(238), 312(238), 313(238), 314(238), 315(238), 317(238), 319(238), 330
 Wright, D., 138(165, 240), 143, 145
- Y**
- Yagupsky, G., 118(243), 122(243), 133(241, 242), 134(242), 136(42, 242), 140, 145, 310(239), 311(189a, 239), 312(189a, 239), 314(189a, 239), 315(189a), 316(239), 318(189a), 319(189a, 239), 321(189a), 322(189a), 328, 330
 Yagupsky, M., 311(189a), 312(189a), 314(189a), 315(189a), 318(189a), 319(189a), 321(189a), 322(189a), 328
 Yamada, R., 414(180), 420(67, 180), 425, 426(67), 443, 446
 Yamamoto, K., 260(240), 299(240), 308(240a), 310(240, 240b, 240c), 330, 370(181), 371(181), 430, 446
 Yamamoto, M., 66(102), 71(67, 102), 83, 84
 Yamamoto, Y., 29, 30, 31, 32(169, 170), 33(169, 170), 34, 35(172), 37(164), 51(166, 167), 60, 65, 74(163, 164, 169, 170), 80(171), 85, 86, 89(246), 90(244), 119(245, 246), 121(245), 127(246a), 145, 182(140), 205
 Yamazaki, H., 29(164), 30, 31, 32(169, 170), 33(169, 170), 34, 35(172), 39(164), 51(166, 167), 74(163, 164, 169, 170), 80(171), 85, 86, 89(246), 119

- (245, 246), 121(245), 127(246a), 137
(247), 145, 334(182), 446
- Yandell, J. K., 174(144a), 205
- Yanezawa, K., 265(214), 329
- Yang, I. C., 218(81), 231, 251, 252
- Yasuda, Y., 148(172), 206
- Yellin, E., 247(73), 251
- Yokokawa, C., 131(232), 145
- Yoon, N. M., 11(32, 33, 34), 19
- Yoshida, T., 31(108), 69(110), 70(110),
71(106, 109, 110), 72(110), 73(110),
74(108, 110), 84
- Yoshimura, J., 434(132), 437(133), 438
(133), 445
- Yoshioka, H., 47(124), 48(124), 80(124),
84
- Young, J. F., 254(241), 304(197), 305(197),
329, 330
- Yurkevich, A. M., 353(142), 368(142), 369
(142), 370(175), 371(142), 372(142),
373(18, 142, 183), 374(18), 419(183),
424(175), 442, 445, 446
- Z**
- Zador, M., 183(38), 202
- Zagalak, B., 420(184), 446
- Zahn, U., 216(52), 217, 218(30), 220(29),
224, 225(14, 15), 226, 227, 228(99),
229, 230(98), 231(8), 233(29), 236(7,
8), 238(99), 239, 241(15, 29), 242
(29), 243(29), 245, 247, 250, 251, 252
- Zaitsev, V. M., 236(60), 251
- Zakharkin, L. I., 126(248), 127(249, 250),
145, 149(120), 155(120), 205
- Zazzetta, A., 344(30), 348(30), 378(30),
442
- Zelesko, M. J., 163(89), 164(91), 171(91),
173(173), 204, 206
- Zhdanov, S. I., 150(41), 203
- Zielinski, F. W., 228(101), 252
- Zimmermann, H., 255(140), 261(140),
327, 334(178), 336(178), 446
- Zweifel, G., 13(38, 39, 41, 42), 14(43),
15(50), 19

Subject Index

A

- Acetylenes
 - reactions with thallium(III) salts, 191-194
 - oxidation to benzils or acyloins, 193
- Acid-base equilibria in organocobalt compounds, 396-397
- Acyl complexes
 - from CO insertion reactions, 90-104, 117-139
 - kinetics and mechanism of formation, 94-97
 - ligand effects, 99-100
 - solvent effects, 97-99
 - stereochemistry, 112-117
 - survey of reactions, 117-139
- Acyl transfer reactions of corrinoids, 425
- Acyl-alkyl rearrangement, on iridium, 110
- Acylimino complexes
 - from metal alkyls and isocyanides, 29, 30
 - protonation, 39
- Alkyl migration mechanism, 113
- Alkylthallium(III) compounds, 173-177
 - decomposition, 175-176
- Amides, from metal alkyls and isocyanides, 29
- Amidinium complexes, from amines and isocyanides, 45
- Amine-boranes, steric effects, 7
- π -Arene complexes, manganese isocyanide, 56
- Aryl iodides, from organothallium compounds, 158, 165
- Arylthallium halides, stability, 164
- Arylthallium trifluoroacetates
 - photolysis, 171
 - preparation, 163-169
 - reactions, 171-173
 - with hydrides, 173
 - with nitrosyl chloride, 170
 - use in organic syntheses, 169-173
 - aryl iodides, 158
 - nitriles, 171

- phenols, 159
- thiophenols, 172
- Auger ionization, 212

B

- π -Benzenechromium tricarbonyl, neutron irradiation, 229
- Bismuth compounds, β -decay to polonium, 235
- Bond breaking, radiochemical studies, 217
- Bonding
 - comparison of CO and RNC, 25
 - isocyanide complexes, 23
- Boranes, historical account, 1-18
- Borohydrides of alkali metals, 5-6
- t*-Butyl isocyanide, nickel complex, 70

C

- Carbene complexes, from isocyanide and alcohols, 40, 46
- Carbodiimides, from azides and isocyanides, 61
- Carbon monoxide, insertion into metal-carbon σ bonds, 87-139
 - cobalt complexes, 131-133
 - effect of alkyl group, 101
 - intermediates, 97
 - iron complexes, 126-130
 - kinetics and mechanism, 94-104
 - ligand effects, 99, 102
 - manganese and rhenium complexes, 122-126
 - molybdenum and tungsten complexes, 118-122
 - nickel, palladium, and platinum complexes, 137-139
 - rhodium and iridium complexes, 133-137
 - ruthenium and osmium complexes, 130-131
 - solvent effects, 97

- Chemical effects of nuclear transformations, 208–249
- Chloroplatinic acid, catalyst for hydrosilylation, 298, 300–302
- Chromium carbene complexes, 52
- Cobalamins, *see also under* Cobalt photochemical reactions, 403
- Cobaloximes, *see also under* Cobalt catalytic reduction, 437
insertion of oxygen, 431
isocyanide derivatives, 63
organo derivatives, 367–374
- Cobalt–carbon σ bonds
cleavage, 401–433
elimination reactions, 408–412, 427–431
effect of ligands, 419–421
homolytic fission, 405
intramolecular displacements, 407–408
insertion reactions, 427–431
oxidation, 432
photochemical reactions, 403–405
reduction, 432
solvent effects, 406
thermolysis, 405
transfer reactions, 421–427
- Cobalt complexes, organic derivatives (*see also* Organo-cobalt complexes), 331–441
cis and trans effects, 349
isomerism, 348
ligand structure, 347
nomenclature, 336–341
reactions, 335, 360–361
synthesis, 350–361, 362–383
 from cobalt(II) compounds, 358
 from cobalt hydrides, 351–358
valence states, 341–342
- Cobalt(I) complexes
addition reactions, 351–358
 acetylenes, 352, 357
 olefins, 352, 356–357
addition to unsaturated compounds, 388–389
alkylation, 353–358
 kinetics, 354
carbonylation, 131–133
with macrocyclic ligands, 384–396
nucleophilic attack, 386–388
reactions with organic halogen compounds, 352, 353–356
 acyl halides, 352
 alkenyl halides, 355
 alkyl halides, 353–355
 alkynyl halides, 355
 aryl halides, 356
 epoxides, 352
 Schiff base complexes, 375–381
- Cobalt(II) complexes, 358–360, 389–390
conversion to organocobalt(III) compounds, 358–360
electron transfer reactions, 389
radical reactions, 389
reactions, 358–360
- Cobalt(III) complexes, 360–361, 390–394
ligand effects, 391–393
nucleophilic attack, 390
- Cobalt corrinoids, 338, 384–386
structures, 341, 345–346
synthesis, 363–364
- Cobalt hydrides, 351
- Cobalt isocyanide derivatives, 63
- Cobalt porphyrins, organic derivatives, 364
- Cobalt silyl complexes, 257–258
in hydrosilylation reactions, 306–307
polynuclear derivatives, 289–290
- Cobinamides, *see also* Organocobalt complexes
isocyanide derivatives, 63
- Copper catalyzed α -additions to isocyanides, 47
- Copper isocyanide complexes, 48, 49, 80
- Copper oxide–isocyanide mixtures as catalysts, 48, 49
- Corrinoids, 338, 384–386
organo derivatives, 384–385
photochemical reduction, 403
reduced forms, 385
 addition to acetylenes, 386
 unsaturated compounds, 385
reactions with alkyl halides, 385
- Cyclohexanone, oxidation by thallium(III) salts, 195–198
- Cyclohexene
oxythallation, 183
stereochemistry, 183

Cyclohexyl isocyanide
addition to methylpalladium complexes,
33
metal complexes, 54
 π -Cyclopentadienylmetal complexes
irradiation, 233–225, 230–232
(C₅H₅)Mn(CO)₃, 217–218, 230–231
Cyclopentadienylthallium, 149–155
organic reactions, 153
preparation of metallocenes, 152–154

D

Dealkylation of isocyanide complexes, 78
Decarbonylation of acyl complexes, 92, 105–
112, 114–117
chemical methods, 111
kinetics and mechanism, 105–110
photolytic, 111
thermal reactions, 105–110
ligand effects, 109
solvent effects, 108–109
 β -Decay, chemical effects, 234–237
Dethallation reaction, 117
Diarylthallium compounds, 157–160
Dibenzenechromium, neutron irradiation,
225
Diborane as reducing agent, 3
hydroboration, 12–14
Dipole moments of transition metal silyls,
288

E

Electron transfer reaction in cobalt(II) com-
plexes, 389
Enzymes containing cobalt corrinoids
isomerase reactions, 441
methyl transfer reactions, 439
 σ - π Equilibria in organocobalt complexes,
399
ESR studies of cobalt isocyanide complexes,
64
Exchange reactions, radiochemical, 219

F

Ferrasilacyclopentane complex, 294
Ferrocene, neutron irradiation, 223

Fluorocarbons, addition to nickel isocya-
nide complexes, 73–74

G

Germanium tetraethyl, irradiation, 218, 222
Gold isocyanide complexes, 41, 80–81
addition of azide, 41

H

Halogenation of organocobalt compounds,
425
Homocysteine, methylation by methylco-
balamin, 426
Homogeneous hydrogenation, catalyzed by
pentacyanocobaltate, 433
mechanism, 435
Homogeneous hydrosilylation, transition
metal catalyzed, 297–310
mechanism, 300–302
Hydroboration, 12–14
Hydrogen-bridged silicon-transition metal
bonds, 290–291
Hydrogen-deuterium exchange, catalyzed
by cobalt cyanide complexes, 438

I

Indenylmolybdenum complexes, carbonyl
insertion, 102
Insertion reactions
carbon monoxide, 88–139
of cobalt-carbon bonds, 427
isocyanides, 28–36
sulfur dioxide, 428
Internal conversion, γ rays, 211
IR and Raman studies, silicon-transition
metal bonds, 285
Iridium alkyls, carbonylation, 97, 102, 115–
116, 135–137
Iridium complexes
acyl-alkyl rearrangement, 110, 115
with isocyanides, 65–68
oxidative addition reactions, 66
with silyl ligands, 259
hydrosilylation, 303–305
stereochemistry, 115

- Iron alkyls, carbonylation, 93, 97, 100, 101, 126–130
- Iron complexes
- carbonyls, 60
 - kinetics and mechanism of reactions, 94
 - with isocyanides, 58–61
 - reactions with nucleophiles, 37–39
 - reactions with isocyanides, 35
 - silyl derivatives, 256
- Isocyanides (isonitriles)
- copper-catalyzed additions, 47–49
 - insertion into metal-carbon bonds, 28–36
- Isocyanide complexes, 21–81
- addition of alkoxide, 40, 42
 - amines, 45
 - hydrazine, 43
 - cobalt, 63–65
 - formation of carbene complexes, 40
 - tetrazole derivatives, 41
- Group VI metal derivatives, 49
- iron, 58–61
 - manganese and rhenium, 54–58
 - nickel, 68–74
 - nucleophilic reactions, 36
 - palladium and platinum, 74–80
 - reaction with azides, 41
 - rhodium and iridium, 65–68
 - ruthenium and osmium, 60, 62
 - structure and bonding, 23
- Isoflavones, synthesis from chalcones, 190

L

- Lanthanide isocyanide complexes, 81
- Lead tetraethyl
- β -decay, 208, 234
 - X-irradiation, 212
- Literature of organotransition metal chemistry, *see* Organotransition metal chemistry

M

- Manganese, neutron capture and decay, 209–210
- Manganese complexes
- carbonylation, 122–125
 - carbonyl halides, reactions with isocyanides, 55
 - decarbonylation of acyl derivatives, 107

- with isocyanides, 54–57
 - electrochemical studies, 27
 - nucleophilic reactions, 37, 38
 - radiochemical studies, 217, 240, 241, 244
 - (C₅H₅)Mn(CO)₃, 217, 230–231
 - Mn₂(CO)₁₀, 229
 - RMn(CO)₅, 232–233
 - with silyl ligands, 255
- Mass spectrometry of silicon-transition metal compounds, 287
- Mechanisms, *see* Reaction mechanisms
- Mercury alkyls
- radiochemistry, 222
 - silyls, in synthesis of transition metal complexes, 265
- Metal-carbon σ bonds
- carbonyl insertion, 88–139
 - radiochemical studies, 221–222
- Metal carbonyls, neutron irradiation, 225–229
- Group VI derivatives, 225–228
 - iron and ruthenium, 229
- Metallocenes, preparation from thallium cyclopentadienide, 152
- Methylcobalamin, photochemistry, 404
- Methyl isocyanide
- reactions with platinum complexes, 77–80
 - reduction by nitrogen-fixing bacteria, 53
- Methylmanganese pentacarbonyl, carbonylation, 113–115
- Methylmercury compounds, formation from organocobalt complexes, 421
- Methyl transfer reactions
- cobalt-containing enzymes, 439
 - organocobalt complexes, 421
- Molybdenum complexes
- carbonylation, 89, 100–102, 118–121
 - with isocyanides, 49–51
 - reactions with isocyanides, 30
 - silylmethyl derivative, 317

N

- Neutron capture and nuclear transformations, 209
- Nickel complexes
- t*-butyl isocyanide, 70
 - carbonylation, 137
 - hydrosilylation, 309–310

Nickel complexes—*continued*

- isocyanides, 68–74
 - IR spectra, 72
 - oxidative addition reactions, 71–73
 - reactions with isocyanides, 29, 32
- Niobium silylmethyl complex, 316
- Nitriles, synthesis, 171
- Nitrosation of organocobalt compounds, 425
- Nitroso compounds, 170
- NMR spectra, silicon-transition metal compounds, 286
 - thallium complexes, 165
- Nonclassical ions, 9
- Norbornyl cations, 10
- Nuclear transformations, chemical effects, 208–220
- Nucleophilic reactions with isocyanide complexes, 36–42

O

- Olefin-cobalt π complexes, 400
- Olefins
 - hydrosilylation, transition-metal catalyzed, 297–310
 - oxidation with thallium(III) nitrate, 187
 - oxythallation, 174–202
 - polymerization by silylmethyl compounds, 322
- Organoarsenic compounds, radiochemical studies, 221
- Organoboranes, reactions, 14–15
- Organocobalt complexes, 331–441
 - acid-base equilibria, 396–397
 - catalytic hydrogenation, 435
 - corrinoids, 384–386
 - σ - π equilibria, 399
 - halogenation, 425
 - macrocyclic complexes, 386
 - nitrosation, 425
 - nomenclature, 336–341
 - preparation, 350–360, 361–383
 - from cobalt(I) complexes, 351–358
 - from cobalt(II) complexes, 358–360
 - from cobalt(III) complexes, 360–361
 - reactions, 396–400
 - photochemical, 403
 - reduction, 432

- stereochemistry, 343–349
 - configuration of cobalt ion, 343
 - isomerism, 348
 - organic ligand, 347
- structural studies, 344
- transalkylation reactions, 421–424
 - to mercury, 421
- Organomercury compounds, from organo-cobalt complexes, 421
- Organosilicon ligands, 253–323
 - heterocyclic derivatives, 293
- Organothallium chemistry, 147–202
- Organothallium(I) compounds, 148–155
- Organothallium(III) compounds, 155–174
 - conversion to aryl iodides, 158
 - nitriles, 171
 - nitroso compounds, 170
 - phenols, 159
 - thiophenols, 172
- Organotransition metal chemistry
 - literature, 447–468
 - reviews, 456–468
- Osmium complexes,
 - carbonylation, 131
 - with silyl ligands, 257
- Oxidative addition reactions,
 - to isocyanide complexes of nickel and palladium, 31
 - of organosilicon compounds, 268–270
- Oxygen (dioxygen), insertion reactions with cobaloxime complexes, 430–431
- Oxythallation reactions, 174–202
 - cyclopropanes, 182
 - olefins, 160, 174–179, 186
 - effect of acetate, 180
 - mechanism, 177, 180–181
 - steroidal olefins, 185

P

- Palladium compounds
 - carbonylation, 137–138
 - reactions with isocyanides, 31–35
- Palladium isocyanide complexes, 74–75
 - addition of alcohols and amines, 46
- Pentacyanocobaltates(III), 333
 - cobalt-carbon bond cleavage, 408–410
 - formation of nitriles, 428
 - homogeneous hydrogenation with, 433

Pentacyanocobaltates(III)—*continued*

- organic derivatives, 381–383
 - reaction with sulfur dioxide, 430
 - synthesis, 394–396
- Phenols from arylthallium trifluoroacetates, 169
- Photochemical reactions of organocobalt compounds, 403
- Photochemical lability of aryl–thallium bond, 171
- Phthalocyanines, organocobalt derivatives, 364
- Platinum compounds
- carbene complexes, 40
 - carbonylation, 138–139
 - silyl complexes, 259–260
 - in hydrosilylation, 302–303
 - silylmethyl complex, 318
- Platinum isocyanide complexes, 75–80
- addition of alcohols and amines, 46
- Polonium compounds, by β -decay of organobismuths, 235, 236
- Polymerization of α -olefins by silylmethyl complexes, 322
- Porphyrins, organocobalt derivatives, 364
- Prethermal reactions in radiochemistry, 242–244
- Pyrazolones, conversion into α,β -acetylenic esters, 200

R

- Radical reactions of cobalt(II) complexes, 389
- Radiochemistry of organometallic compounds, 207–249
- germanium tetraethyl, 218, 222
 - metal–carbon σ bonds, 221–223
 - organoarsenic compounds, 221–222
 - organomercury compounds, 222
- Radioisotope enrichment, 216
- Reaction mechanisms
- carbonyl insertion, 94–104
 - effect of solvent, 97
 - nature of intermediate, 97–99
 - hydrosilylation, 300
 - reduction by pentacyanocobaltate, 435–437
 - free radicals, 436

intermediate organocobalt compounds, 435

- Reactivity of β -carbon in organocobalt compounds, 397–399
- Recoil energy, γ emission, 210
- Reducing agents, complex hydrides, 11
- Reduction of organocobalt complexes, 432
- Rhenium complexes
- carbonylation, 125–126
 - with isocyanides, 57–58
- Rhodium complexes
- carbonylation, 133–135
 - as decarbonylation reagent [RhCl(PPh₃)₃], 111
 - with isocyanides, 65–58
 - oxidative addition reactions, 66
 - silyls, 258
 - in hydrosilylation, 305
- Rhodium dicyclopentadienyl, 236
- Ribonuclease triphosphate, reduction by dithiols, 441
- Ruthenium carbonyl [Ru₃(CO)₁₂], neutron irradiation, 229
- Ruthenium complexes
- carbonylation, 130
 - with organosilicon ligands, 257
- Ruthenocene
- from ferrocene and uranium fission reactions, 237
 - neutron irradiation, 224

S

- Scavengers in radiochemical reactions, 246
- Schiff bases, organo-cobalt complexes, 376–381
- Separation-induced reactions, 241
- Silicon-transition metal bonds, 253–297
- addition at silicon, 279
 - at transition metal, 280
 - back-bonding, 282–283
 - cleavage, 273–279
 - with chloroalkanes, 276
 - halogens, 276
 - hydrogen, 276
 - by reductive elimination, 277
 - solvolysis, 273–275
 - transmetallation, 278
- dimensions, 281–282

- Silicon-transition metal bonds—*continued*
hydrogen-bridged, 290–291
insertion reactions, 278–279
ligand exchange, 281
substitution
at metal, 271–273
at silicon, 270–271
Siloxo-metal derivatives, 296–297
Silyl-transition metal complexes, 253–323
anionic derivatives, 295–296
IR and Raman studies, 285
mass spectrometry, 287
NMR studies, 286
synthesis, 263–270
by amine elimination, 267
by hydrogen elimination, 265–266
by hydrogen halide elimination, 267
metathetical reactions, 263–264
oxidative addition or elimination, 268–269
from silylmercurials, 265
Silylene (R_2Si) complexes, 291–293
Silylmethyl group, transition metal derivatives, 310–323
polymerization of α -olefins, 322
reactions, 321
synthesis, 318–321
Solvolysis, steric effects in, 8
Speier's catalyst for hydrosilylation, 298
Stereochemistry
of carbonylation reactions, 112
decarbonylation, 112
organocobalt(III) complexes, 343–349
Structural studies
isocyanide complexes, 23
metal-silyl complexes, 261–262, 280–281
 $Co(CO)_4(SiCl_3)$, 283
 $FeH(SiCl_3)_2(CO)$ ($\pi-C_5H_5$), 284
 $RhHCl(SiCl_3)(PPh_3)_2$, 284
organocobalt(III) complexes, 344
Substituent effects on Co–C bond cleavage, 412
Sulfur dioxide, reaction with pentacyanocobaltate, 430
Szilard–Chalmers reaction, 207–216
- T**
- Technetium compounds, radiochemical syntheses, 232
Tetracyanoethylene, reactions with isocyanide complexes, 66
Tetrazole complexes, from azides and isocyanide complexes, 41
Thallation reactions, 161–202
isomer distribution, 166
kinetic studies, 168
orientation dependence on reaction conditions, 169
reversibility, 165
Thallium ions, 183–185
Thallium cyclopentadienide, 149
derivatives, 151–155
Thallium(I) halides, reactions with Grignard or organo-lithium reagents, 148
Thallium(III) nitrate (TTN), 187
as an oxidizing agent, 187–202
acetylenes, 191–194
aldehydes and ketones, 195
chalcones, 189
cyclohexanone, 195–198
enamines, 200
enolized carbonyl compounds, 199
 β -keto esters, 201
olefins, 187
Thallium in organic chemistry, 147–202
Thallium(III) organic compounds, 155–202
alkyl derivatives, 173
conversion
to aryl iodides, 158
to phenols, 159
formation from organocobalt complexes, 424
preparation
(R_3Tl), 155–156
(R_2TlX), 156–158
($RTlX_2$), 160–163
Thallium(III) salts as oxidants, 174
Thallium(III) trifluoroacetate (TTFA), 163–173
kinetic studies, 168
as thallation reagent, 163
Thermal reactions, in radiochemistry, 238
Transalkylation reactions
cobalt to mercury, 421
cobalt to palladium, 424–425
cobalt to thallium, 424
Transfer of organic groups from organocobalt complexes, 421–427

d-d Transitions in organocobalt complexes,
350

Transmetallation reactions,
silicon-transition metal complexes, 278
with thallium, 169

Trimethylsilylmethyl group (Me_3SiCH_2)
trans influence, 317
transition metal complexes, 310–323
reactions, 321–323
synthesis, 318–321

Tungsten complexes, carbonylation, 121–
122
with isocyanides, 49

U

Uranium borohydride, 4
Uranium isocyanide complexes, 81

V

Vinyl isocyanide complexes with manga-
nese, 57
Vitamin B_{12} , reaction with isocyanides, 63
structure, 332

Cumulative List of Contributors

- Abel, E. W., **5**, 1; **8**, 117
 Aguiló, A., **5**, 321
 Armitage, D. A., **5**, 1
 Atwell, W. H., **4**, 1
 Bennett, M. A., **4**, 353
 Birmingham, J., **2**, 365
 Brook, A. G., **7**, 95
 Brown, H. C., **11**, 1
 Brown, T. L., **3**, 365
 Bruce, M. I., **6**, 273; **10**, 273, **11**, 448
 Cais, M., **8**, 211
 Cartledge, F. K., **4**, 1
 Chalk, A. J., **6**, 119
 Churchill, M. R., **5**, 93
 Coates, G. E., **9**, 195
 Collman, J. P., **7**, 53
 Coutts, R. S. P., **9**, 135
 Coyle, T. D., **10**, 237
 Craig, P. J., **11**, 332
 Cullen, W. R., **4**, 145
 Cundy, C. S., **11**, 253
 de Boer, E., **2**, 115
 Dessy, R. E., **4**, 267
 Emerson, G. F., **1**, 1
 Ernst, C. R., **10**, 79
 Fritz, H. P., **1**, 239
 Fuson, R. C., **1**, 221
 Gilman, H., **1**, 89; **4**, 1; **7**, 1
 Green, M. L. H., **2**, 325
 Griffith, W. P., **7**, 211
 Gubin, S. P., **10**, 347
 Gysling, H., **9**, 361
 Harrod, J. F., **6**, 119
 Heck, R. F., **4**, 243
 Heimbach, P., **8**, 29
 Hieber, W., **8**, 1
 Jolly, P. W., **8**, 29
 Kaesz, H. D., **3**, 1
 Kettle, S. F. A., **10**, 199
 Kilner, M., **10**, 115
 King, R. B., **2**, 157
 Kingston, B. M., **11**, 253
 Kitching, W., **4**, 267
 Köster, R., **2**, 257
 Kühlein, K., **7**, 241
 Kuivila, H. G., **1**, 47
 Kumada, M., **6**, 19
 Lappert, M. F., **5**, 225; **9**, 397; **11**, 253
 Luijten, J. G. A., **3**, 397
 Lupin, M. S., **8**, 211
 McKillop, A., **11**, 147
 Maddox, M. L., **3**, 1
 Maitlis, P. M., **4**, 95
 Manuel, T. A., **3**, 181
 Mason, R., **5**, 93
 Moedritzer, K., **6**, 171
 Morgan, G. L., **9**, 195
 Mrowca, J. J., **7**, 157
 Nagy, P. L. I., **2**, 325
 Nesmeyanov, A. N., **10**, 1
 Neumann, W. P., **7**, 241
 Okawara, R., **5**, 137
 Oliver, J. P., **8**, 167
 Onak, T., **3**, 263
 Parshall, G. W., **7**, 157
 Paul, I., **10**, 199
 Pettit, R., **1**, 1
 Poland, J. S., **9**, 397
 Pratt, J. M., **11**, 332
 Prokai, B., **5**, 225
 Rijkens, F., **3**, 397
 Ritter, J. J., **10**, 237
 Rochow, E. G., **9**, 1
 Roper, W. R., **7**, 53
 Rubezhov, A. Z., **10**, 347
 Schmidbaur, H., **9**, 259
 Schrauzer, G. N., **2**, 1
 Schwebke, G. L., **1**, 89
 Skinner, H. A., **2**, 49
 Slocum, D. W., **10**, 79
 Stafford, S. L., **3**, 1
 Stone, F. G. A., **1**, 143
 Tamao, K., **6**, 19
 Taylor, E. C., **11**, 147
 Thayer, J. S., **5**, 169
 Todd, L. J., **8**, 87
 Treichel, P. M., **1**, 143; **11**, 21
 Tsutsui, M., **9**, 361

Tyfield, S. P., **8**, 117
van der Kerk, G. J. M., **3**, 397
Wada, M., **5**, 137
Wailes, P. C., **9**, 135
West, R., **5**, 169

Wiles, D. R., **11**, 207
Wilke, G., **8**, 29
Wojcicki, A., **11**, 88
Ziegler, K., **6**, 1
Zuckerman, J. J., **9**, 21

Cumulative List of Titles

Alkali Metal Derivatives of Metal Carbonyls, **2**, 157
Alkyl and Aryl Derivatives of Transition Metals, **7**, 157
Alkylcobalt and Acylcobalt Tetracarbonyls, **4**, 243
Allyl Metal Complexes, **2**, 325
 π -Allynickel Intermediates in Organic Synthesis, **8**, 29
Applications of ^{119}mSn Mössbauer Spectroscopy to the Study of Organotin Compounds, **9**, 21
Boranes in Organic Chemistry, **11**, 1
Carboranes and Organoboranes, **3**, 263
Catalyses by Cobalt Carbonyls, **6**, 119
Catenated Organic Compounds of the Group IV Elements, **4**, 1
Conjugate Addition of Grignard Reagents to Aromatic Systems, **1**, 221
Cyclobutadiene Metal Complexes, **4**, 95
Cyclopentadienyl Metal Compounds, **2**, 365
Diene-Iron Carbonyl Complexes, **1**, 1
Electronic Effects in Metallocenes and Certain Related Systems, **10**, 79
Electronic Structure of Alkali Metal Adducts of Aromatic Hydrocarbons, **2**, 115
Fast Exchange Reactions of Group I, II, and III Organometallic Compounds, **8**, 167
Fluorocarbon Derivatives of Metals, **1**, 143
Heterocyclic Organoboranes, **2**, 257
 α -Heterodiazalkanes and the Reactions of Diazoalkanes with Derivatives of Metals and Metalloids, **9**, 397
Infrared Intensities of Metal Carbonyl Stretching Vibrations, **10**, 199
Infrared and Raman Studies of π -Complexes, **1**, 239
Insertion Reactions of Compounds of Metals and Metalloids, **5**, 225
Insertion Reactions of Transition Metal-Carbon σ -Bonded Compounds I: Carbon Monoxide Insertion, **11**, 88
Isoelectronic Species in the Organophosphorus, Organosilicon, and Organoaluminum Series, **9**, 259
Keto Derivatives of Group IV Organometalloids, **7**, 95
Lewis Base-Metal Carbonyl Complexes, **3**, 181
Ligand Substitution in Transition Metal π -Complexes, **10**, 347
Literature of Organo-Transition Metal Chemistry 1950–1970, **10**, 273
Literature of Organo-Transition Metal Chemistry 1971, **11**, 448
Mass Spectra of Metallocenes and Related Compounds, **8**, 211
Mass Spectra of Organometallic Compounds, **6**, 273
Metal Carbonyl Cations, **8**, 117
Metal Carbonyls, Forty Years of Research, **8**, 1
Metal π -Complexes Formed by Seven- and Eight-Membered Carbocyclic Compounds, **4**, 353
Nitrogen Groups in Metal Carbonyl and Related Complexes, **10**, 115
Nitrosyls, **7**, 211
Nuclear Magnetic Resonance Spectra of Organometallic Compounds, **3**, 1
Of Time and Carbon-Metal Bonds, **9**, 1

- Olefin Oxidation with Palladium Catalyst, **5**, 321
Organic Chemistry of Lead, **7**, 241
Organic Complexes of Lower-Valent Titanium, **9**, 135
Organic Substituted Cyclosilanes, **1**, 89
Organoarsenic Chemistry, **4**, 145
Organoberyllium Compounds, **9**, 195
Organolanthanides and Organoactinides, **9**, 361
Organometallic Aspects of Diboron Chemistry, **10**, 237
Organometallic Chemistry, A Forty Years' Stroll, **6**, 1
Organometallic Chemistry, My Way, **10**, 1
Organometallic Chemistry of Nickel, **2**, 1
Organometallic Chemistry, Some Personal Notes, **7**, 1
Organometallic Complexes with Silicon-Transition Metal or Silicon-Carbon-Transition Metal Bonds, **11**, 253
Organometallic Nitrogen Compounds of Germanium, Tin, and Lead, **3**, 397
Organometallic Pseudohalides, **5**, 169
Organometallic Reaction Mechanisms, **4**, 267
Organopolysilanes, **6**, 19
Organosulphur Compounds of Silicon, Germanium, Tin, and Lead, **5**, 1
Organothallium Chemistry, Recent Advances, **11**, 147
Organotin Hydrides, Reactions with Organic Compounds, **1**, 47
Oxidative-Addition Reactions of d^8 Complexes, **7**, 53
Preparation and Reactions of Organocobalt(III) Complexes, **11**, 332
Redistribution Equilibria of Organometallic Compounds, **6**, 171
Radiochemistry of Organometallic Compounds, **11**, 207
Strengths of Metal-to-Carbon Bonds, **2**, 49
Structural Aspects of Organotin Chemistry, **5**, 137
Structural Chemistry of Organo-Transition Metal Complexes, **5**, 93
Structures of Organolithium Compounds, **3**, 365
Transition Metal-Carborane Complexes, **8**, 87
Transition Metal-Isocyanide Complexes, **11**, 21